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UNIVERSITY OF ALBERTA

REMOVAL OF LOW CONCENTRATIONS OF CHLORINATION BY-PRODUCTS USING ACTIVATED CARBON

BY

ROBERT C. ANDREWS

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA
SPRING 1990

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled REMOVAL OF LOW CONCENTRATIONS OF CHLORINATION BY-PRODUCTS USING ACTIVATED CARBON submitted by ROBERT C. ANDREWS in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY in ENVIRONMENTAL ENGINEERING.

Supervisor

Daniel W. Smith

D. T. Williams

External Examiner

Date April 23, 1990

DEDICATION

This dissertation is dedicated to the memory of:

Adelaide Andrews
and
Tara Andrews

for providing inspiration which will last a lifetime.

ABSTRACT

Technologies concerning the removal of organic compounds in drinking water, especially those formed upon chlorination, are a matter of great importance in the water treatment industry. Computer modelling was evaluated in terms of predicting breakthrough of trihalomethanes in a full-scale water treatment plant employing granular activated carbon (GAC). Adsorption isotherm experiments were used to quantify competition from background organics and to assess the importance for trihalomethane adsorption of the slow fouling of GAC by natural organic substances. This fouling effect caused adsorptive capacity to decrease as a function of time due to the slow adsorption of background material. The Equilibrium Column Model was found useful in predicting chloroform breakthrough for two different carbons and two operating seasons. Results from experiments with pre-loaded carbon suggest that the observed reduction in capacity for trihalomethanes in the lower half of full-scale beds may be largely due to blockage of adsorption sites by pre-adsorbed background organics.

Quantitation of the removal capacity of GAC for the mutagenic compound MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] was examined under conditions representative of typical water treatment practice and attempts made to identify the removal mechanism. Isotherm experiments were conducted using both virgin carbon and carbon which had been pre-loaded with natural organic material. MX was shown to be very well removed over a wide

concentration range although, as observed for trihalomethanes, a significant reduction in capacity was observed for the pre-loaded carbon. To illustrate that an adsorption mechanism was involved in the removal of MX from water using activated carbon, various combinations of solvents and desorption conditions were examined in attempts to recover MX from activated carbon. While the removal of MX, is at least in part, attributable to adsorption, some reaction to other compounds does occur. Three of these compounds have been identified.

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List of Abbreviations

$1/n_i$ = Freundlich intensity constant for component i

A = cross sectional area or specific surface area of the adsorbent

ALS = automated liquid sampler

APE = average percentage error

BVF = bed volumes fed

BVF_i = bed volumes fed to breakthrough for component i

C = equilibrium concentration

C_{0k} = influent concentration of component k

Ceca 830 = Cecacarbon 830® activated carbon

CH_2Cl_2 = dichloromethane

CCl_4 = carbon tetrachloride

$CHBr_3$ = bromoform

$CHCl_2Br$ = bromodichloromethane

$CHCl_3$ = chloroform

$CHClBr_2$ = dibromochloromethane

CI = confidence interval

C_i = observed concentration of component i at equilibrium

$\hat{C}_i$ = predicted concentration of component i at equilibrium

APE = average percentage error

$C_{i,k-1}$ = liquid-phase concentration of component i in zone k-1

C_i^o = single solute liquid phase concentration in equilibrium with q_i^o

C_{io} = initial concentration of component i

DAI = direct aqueous injection

DCM = dichloromethane

DOC = dissolved organic carbon

ε = bed void fraction

EBCT = empty bed contact time

EC = electron capture

ECD = electron capture detector

ECM = equilibrium column mode

EMX = 2-chloro-3-(dichloromethyl)-4-oxo-butenoic acid

EtOac = ethyl acetate

eV = electron volts

F-100 = Filtrasorb 100® activated carbon

F-300 = Filtrasorb 300® activated carbon

F-400 = Filtrasorb 400® activated carbon

FID = flame ionization detector

GAC = granular activated carbon

GC = gas chromatograph or gas chromatography

GC/ECD = gas chromatography with electron capture detection

GC/FID = gas chromatography with flame ionization detection

GC/MS = gas chromatography with mass spectral detection

HC = hypothetical components

HCFP = hypothetical component fitting program

HSDM = homogeneous surface diffusion model

IAST = ideal adsorbed solution theory

IC = inorganic carbon

ID = internal diameter

$K(t)$ = Freundlich capacity at time, t

K_0 = initial Freundlich capacity

$K_{1,2,3,4}$ = Freundlich capacity at time, $t_{1,2,3,4}$

K_i = Freundlich isotherm capacity constant for component i

LLS = linear least squares

LSC = liquid sample concentrator

LUCA = layered upflow carbon adsorption

M = moles

m/v = mass per volume ratio

MBA = mucobromic acid

MeOH = methanol

MX = 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone

MX+EMX = solution containing both MX and EMX

MX/EMX = MX and/or EMX

N = number of components in mixture or number of data points

n_i = inverse of the Freundlich parameter 1/n for component i

NLLS = non-linear least squares

NMR = nuclear magnetic resonance

NOM = natural organic matter

NVOC = non-volatile organic carbon

OC = organic carbon

PGAC = powdered granular activated carbon

pre-GAC = prior to granular activated carbon treatment

PSDM = pore surface diffusion model

Q = equilibrium capacity

q = solid phase concentration

q_i = solid phase concentration of component i

$q_{i,k-1}$ = solid-phase concentration of component i in zone k-1

q_i^o = single solute solid phase concentration for component i, evaluated at the spreading pressure of the mixture

q_T = total surface loading

R = universal gas constant

ρ_B = bulk density of bed

SCAM = simplified competitive adsorption model

SSE = sum of squares of errors

T = absolute temperature

TC = total carbon

TCP = trichlorophenol

TCT = tetrachlorotoluene

THM = trihalomethane

TOC = total organic carbon

TOX = total organic halide

TTHM's = total trihalomethanes

V = volume

v/v = volume per volume ratio

V_f = interstitial fluid velocity

VOC = volatile organic compound

V_{wi} = velocity of wavefront for component i

Vw_{k-1} = velocity of the wave front between zones k-1 and k

$X_{observed}$ = observed liquid or solid phase concentration at equilibrium

$X_{predicted}$ = predicted liquid or solid phase concentration at equilibrium

z_i = mole fraction of component i adsorbed on carbon surface

π_i^o, π_j^o = spreading pressure of single solute components i, j

π_m = spreading pressure of the mixture

1.0 INTRODUCTION

The use of activated carbon in either granular (GAC) or powdered form is a well known removal technology for organic substances including trihalomethanes which are formed as chlorination by-products. The use of GAC can be, however, costly and the adsorption processes are very complex: under water treatment conditions the removals obtainable cannot be quantitatively predicted from theoretical considerations. It is important, however, to obtain a reliable estimate of the capability of GAC to successfully handle a given organics problem, before an implementation decision is made.

Mutagenicity testing has been applied to drinking water in the last few years to assist in assessing organic compounds of health concern which may either be present in the raw water or produced during the treatment process. Chlorine, the disinfectant used most frequently in North America drinking water treatment practice has been shown in numerous studies to produce mutagenicity (Noot et al., 1989). Until recently, however, most of the mutagenicity could not be related to specific compounds. Within the last several years the compound MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] has been shown to be responsible for up to 57% of the acid fraction mutagenicity observed in chlorinated drinking water (Hemming et al., 1986; Kronberg and Vartiainen, 1987; Meier et al., 1987; Horth et al., 1987; Kronberg and Christman, 1988).

The use of granular activated carbon (GAC) has been demonstrated to be an effective means of removing mutagenic compounds produced during chlorination of drinking water (Monarca et al., 1983; Loper et al., 1985; Huck, 1986; Huck et al., 1988) and as such could be a useful treatment to remove MX. Quantitation of the removal of mutagenicity by GAC has however been generally limited to reporting either percentage reduction or breakthrough for various numbers of bed volumes treated.

Computer adsorption models which are currently available allow laboratory data to be used in the design of full scale GAC adsorbers. These models can predict competition among adsorbing substances, including the effect of "background" organics which is important in real applications. Results from these models may then be used to predict, within certain limits, the performance of full scale adsorbers. The simplest models, which utilize the most easily obtainable input data, ignore mass transfer considerations, while the more sophisticated models take them into account. Simple models can however be utilized to predict estimates of breakthrough.

Because of its high cost there are very few full scale granular activated carbon installations for drinking water treatment in North America. In the summer of 1985 the first full scale GAC contactors at a large Canadian water treatment plant were put into operation. This system is located at the Buffalo Pound water treatment plant which serves the cities of Regina and Moose Jaw, Saskatchewan. These contactors follow conventional treatment and were installed primarily to remove algal-related taste and odour problems. Reduction of the relatively high trihalomethane levels was also a consideration, even though these values do not exceed current regulatory guidelines.

The first phase of this research was developed to take advantage of this unique installation to obtain information which would be of value to the industry in general as well as to Buffalo Pound. Major areas of study were therefore directed towards quantifying the importance for trihalomethane adsorption of the slow fouling of GAC by background natural organic substances and to compare observed trihalomethane removals in full scale contactors to modelling predictions based on isotherm experiments.

The second phase of this research examined the occurrence and removal of MX in conventional drinking water practice and attempted to quantify the removal capacity of GAC for MX under representative water treatment conditions. Attempts to desorb MX from activated carbon using various solvents and displacer compounds were undertaken to assist in investigating the governing removal mechanism.

2.0 LITERATURE REVIEW

Under water treatment conditions adsorption processes on GAC are very complex and are influenced greatly by fluctuations of influent parameters. Phenomena such as competitive adsorption, catalytic effects on oxidant-organic reactions, and seasonal temperature, pH, and background organic matrix changes make predictions of removal capacities for individual contaminants difficult. To obtain meaningful estimates in a short period of time requires the use of numerical models. The use of these models combined with experimental isotherm results allows the prediction of multicomponent competitive equilibria of known organic compounds in background mixtures of unknown composition. A great deal of information has been published concerning the use of GAC in water treatment, e.g. Suffet and McGuire (1981), AWWARF (1983a), AWWARF (1983b), Sontheimer et al. (1988).

This section describes the basis of evaluating adsorption of trihalomethanes and mutagenic compounds in the presence of an unidentified background matrix containing natural organic matter and the application of computer modelling to adsorption processes.

2.1 Competitive Adsorption Effects

Background organics can have a major impact on the adsorption of specific compounds on GAC. Prior to investigations conducted by Narbaitz and Benedek (1986), Crittenden et al. (1985c) and Frick and Sontheimer (1983) the study of multicomponent adsorption was limited to known mixtures of similar compounds. Earlier studies

(Fritz and Schlünder, 1981; Fritz et al., 1981) examined the competitive adsorption of bi-solute mixtures on activated carbon. These bi-solute mixtures were subdivided into three groups with respect to adsorption equilibrium and rate behavior. The authors found that the use of Ideal Adsorbed Solution Theory (IAST) permitted rapid prediction of bi-solute equilibria.

Other predictive modelling has involved only competitive interactions attributable to known mixtures (Crittenden et al., 1980; Thackar et al., 1983; Kong and DiGiano, 1986). Both Thackar et al. (1983) and Crittenden et al. (1980) conducted studies using computer models to predict competitive displacement of adsorbed compounds in GAC beds. In model simulations, desorption resulting from competition was shown to cause effluent concentrations of chloroform and bromodichloromethane to exceed influent concentrations for prolonged periods of time (Thackar et al., 1983). Such an effect was also reported by Merk et al. (1980), Balzli et al. (1978) and Famularo et al. (1980). Kong and DiGiano (1986) evaluated competitive interactions among three volatile organic compounds; trichloroethylene, tetrachloroethylene and carbon tetrachloride on Filtrasorb 400® activated carbon and XE-340 carbonaceous resin. Description of competitive adsorption behavior using the IAST model was found adequate for some but not all of the equilibrium data. The agreement between predicted and observed data was shown to depend on the accuracy of single-solute isotherm parameters, the accuracy of measuring aqueous concentrations and the adequacy of the experimental design to detect competitive interactions. Recommendations for further work included the use of large sample volumes (on the order of a few hundred milliliters) such that both the adsorbent dosages and initial concentrations could be reduced to a range of practical interest where competitive effects could most appropriately be measured. Similar studies involving carbon tetrachloride and five other toxic or carcinogenic compounds were conducted by Weber and Pirbazari (1982) in both the presence and absence of background organics as represented using humic acid. The reduction in capacity attributed to competition from background organics may be assessed by the change in the Freundlich capacity parameter (K) (Table 2.1). The presaturated carbon designation condition was used to illustrate, for carbon tetrachloride, the adverse effect on adsorptive capacity of using carbon which had been saturated with humic acid prior to use.

Investigations conducted by Murin and Snoeyink (1979) showed that background organics, mainly composed of humic substances, competed with toxic organics and greatly reduced adsorptive capacities. Although some studies have used humic acid solutions to simulate natural organic matter, Herzing et al. (1977) have shown that isotherms obtained using well water containing natural organic compounds were not the same as those obtained using humic acid solutions since the nature of the organic material differed. Malcolm and MacCarthy (1986) concluded on the basis of ^{13}C NMR data that commerically available humics were not representative of soil or water humic or fulvic acids and should not be used as analogues of soil and water humic substances. Therefore, evaluation of the adsorptive capacity of GAC for specific compounds under treatment plant conditions may require the use of the actual water with its complex background organic matrix.

Narbaitz and Benedek (1986) presented one of the first attempts to apply competitive adsorption to a truly practical case. The capacity of activated carbon for 1,1,2-trichloroethane was found to be reduced in the presence of background organics as represented by a sample of river water. In studies conducted by Crittenden et al. (1985c) equilibrium competitive interactions between individual components and unknown mixtures were described and verified using an actual groundwater.

Najm et al. (1990) evaluated the reduction in PAC adsorptive capacity resulting from background organics for 2,4,6-trichlorophenol (TCP), by using a groundwater which contained 3 mg/L dissolved organic carbon (DOC). A reduction in capacity of 50% was observed following a 20 minute contact period. Murin and Snoeyink (1979) reported a 60% reduction in capacity for TCP in the presence of humic acid at a DOC concentration of 10 mg/L.

Some estimation of the extent to which competition occurs should be considered in the design of activated carbon adsorbers (Munz et al., 1988; Zimmer et al., 1987b). It has been suggested that DOC may be used as a surrogate to measure the largest fraction of background organic matter, typically humic material (Munz et al., 1988). Volatile hydrocarbons have been shown to represent only a small percentage of this heterogeneous humic material (Zimmer et al., 1987b). The use of ozonation, by increasing biodegradability, may potentially reduce loadings of adsorbable DOC and correspondingly the extent of competition for adsorption sites (Maloney et al., 1985; Wang and DiGiano, 1988).

Table 2.1 - Effect of Background Organics on Adsorptive Capacity for Six Organic Coumpounds (After Weber and Pirbazari, 1982)

Compound	Range of Ce (μg/L)	Background Conditions	K (μg/g)	1/n	r (a)
Benzene	5-500	OFW	1140	0.40	0.987
		HAS	810	0.51	0.992
Carbon tetrachloride	0.1-1000	OFW	210	0.68	0.965
		HAS	260	0.67	0.987
		Presat. Carbon	170	0.52	0.992
p-Dichlorobenzene	5-5000	OFW	17100	0.37	0.997
		HAS	16300	0.39	0.986
1,2-Dichloroethane	1.0-100	Ohio R. Wat.	50	0.83	
Dieldrin	0.2-50	OFW	2740	0.56	0.917
		HAS	1460	0.68	0.977
PCB (Aroclor 1016)	0.5-100	OFW	3440	0.66	0.897
		HAS	3160	0.56	0.991
PCB (Aroclor 1254)	0.5-50	OFW	730	1.14	0.977
		HAS	1020	0.74	0.959

(a) r = Correlation coefficient for fit of the linearized Freundlich isotherm equation to the experimental data.

OFW = Organic free water
HAS = Humic acid solution

2.1.1 Pre-Loading Effects

Adsorption of background organic material over a period of time has been shown to create capacity reduction problems in addition to the reduction in adsorptive capacity, due to competitive adsorption for volatile organic compounds (VOCs) (Munz et al., 1990; Munz et al., 1988, Zimmer et al., 1987b; Summers et al., 1989). Background organic material consists of both anthropogenic organic matter and natural organic matter, the relative concentration of which will depend on the specific water source. The reduction in capacity which results from the slow adsorption of natural organic matter (NOM), over time has been described as "fouling", "preadsorption" or "pre-loading" (Summers et al., 1989; Munz et al., 1990).

The NOM adsorbs much more slowly than other organic contaminants of interest due to its generally larger molecular size. To a substantial extent it adsorbs irreversibly. Because the NOM is present at a much higher concentration than specific contaminants, it can break through to lower segments of GAC beds prior to a specific contaminant. It then "pre-loads" or "fouls" the carbon in these segments, substantially reducing its useful adsorptive capacity as shown by Munz et al. (1990) (Figure 2.1). These findings have a significant impact on the way in which GAC adsorbers should be designed and operated for maximum efficiency.

Zimmer et al. (1987b) showed experimentally that the adsorptive capacity of carbon as represented by the Freundlich K for selected compounds decreased as a function of the time that the carbon had been "pre-loaded" with background organics. The carbon

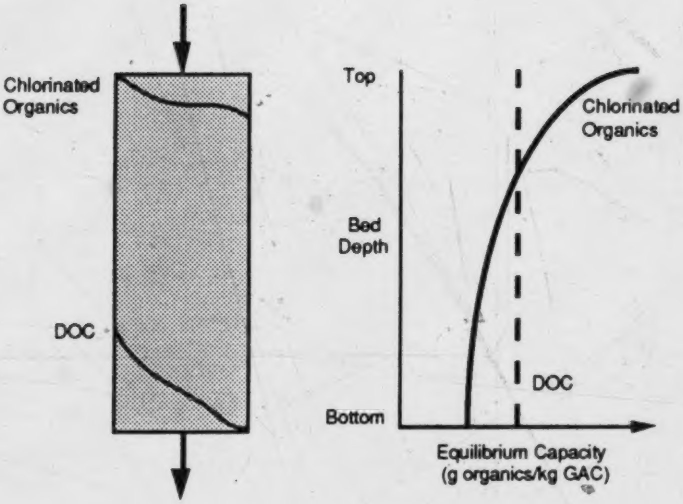

Chlorinated Organics
DOC
Top
Bed Depth
Bottom
Chlorinated Organics
DOC
Equilibrium Capacity (g organics/kg GAC)

Figure 2.1 Effect of DOC Pre-Loading on Adsorptive Capacity (Adapted from Munz et al., 1990)

itself was pre-loaded using a small (10 cm) fixed bed, and carbon samples were removed after various times of exposure. Isotherm analyses were performed for three chlorinated hydrocarbons: 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene. The authors hypothesized that an enrichment of the more strongly adsorbing fraction of the humic substances on the carbon over time would cause a further reduction in micropollutant adsorptive capacity. They also suggested that the breakthrough of specific micropollutants in treatment plants could be calculated by models which incorporated a Freundlich K parameter which decreased with respect to time.

Later, Zimmer et al. (1988) compared the reduction in Freundlich K for trichloroethane in two groundwaters, using carbon obtained from both a "pre-loading" column and from three depths in a full-scale adsorber. The reduction in Freundlich K's were similar for the two groundwaters and the full-scale adsorbers.

Co-adsorption studies conducted by Summers et al. (1989, 1988) comparing distilled water and Rhine River water which contained NOM showed that the presence of NOM had little impact on the adsorption capacity for trichloroethane. In order to assess the reduction in capacity attributable to the pre-loading with NOM, the same authors conducted isotherm experiments using carbon obtained from various bed depths in pilot scale columns. Following a short operational period (4 weeks) the carbon near the top of the bed was observed to be most affected by fouling. As operational times increased, trichloroethane isotherms using pre-loaded carbon from all depths approached capacities obtained from the deepest bed depth (1.5 m). The rapid decrease in capacity at the shallow depths (0.28 m) differed from observations reported for groundwater (Zimmer et al., 1987b; Zimmer et al., 1988) where fouling occurred much more slowly. Summers et al. (1989) observed very close agreement between data obtained using pre-loaded GAC isotherms and column tests, suggesting that isotherm tests may be useful in predicting the characteristics of actual GAC contactors. Hand et al. (1989) reported data for pilot studies which evaluated the breakthrough of dichloroethene and trichloroethene. Competitive interactions could be explained using IAST. Numerical models which were used to predict breakthrough data considered only the effect of NOM in reducing kinetics and not in reducing capacity.

Studies conducted by Baldauf (1986) using groundwater, presented trichloroethylene capacity data for a GAC filter as a function of filter bed depth (Figure 2.2). The capacity obtained in each section of the bed for both a breakthrough of 10% of the influent concentration and at exhaustion is shown. Much lower capacities were achieved in the lower bed segments, even at exhaustion. This reduction in capacity was attributed to the fouling of the carbon by the natural orgainc matter, which had an opportunity to adsorb in the lower bed depths before trichloroethylene which was more strongly adsorbed.

Baldauf (1986) also reported results from pilot scale investigations in which a fixed bed reactor was compared to an upflow reactor. The final bed height was the same in both reactors, but in the upflow reactor the initial bed height was lower. In the upflow reactor, additional layers of carbon were added as

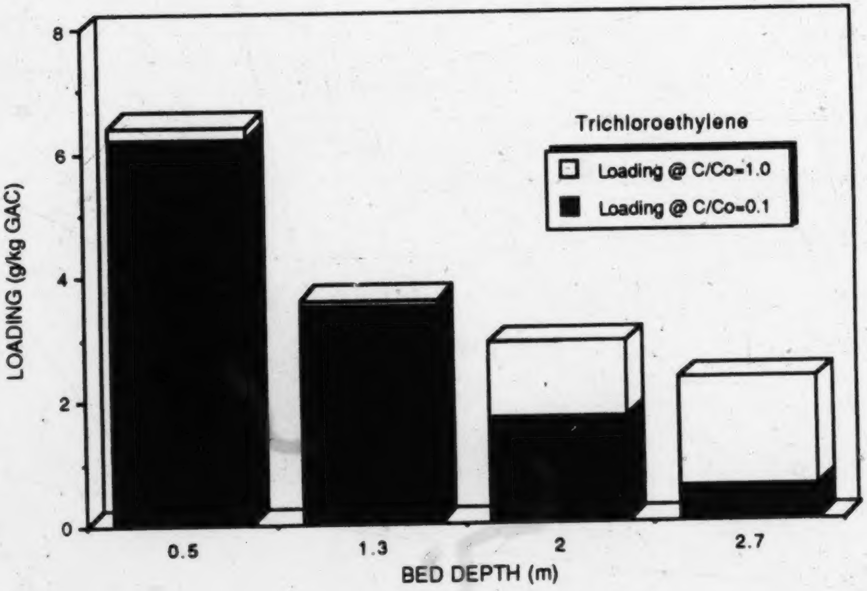
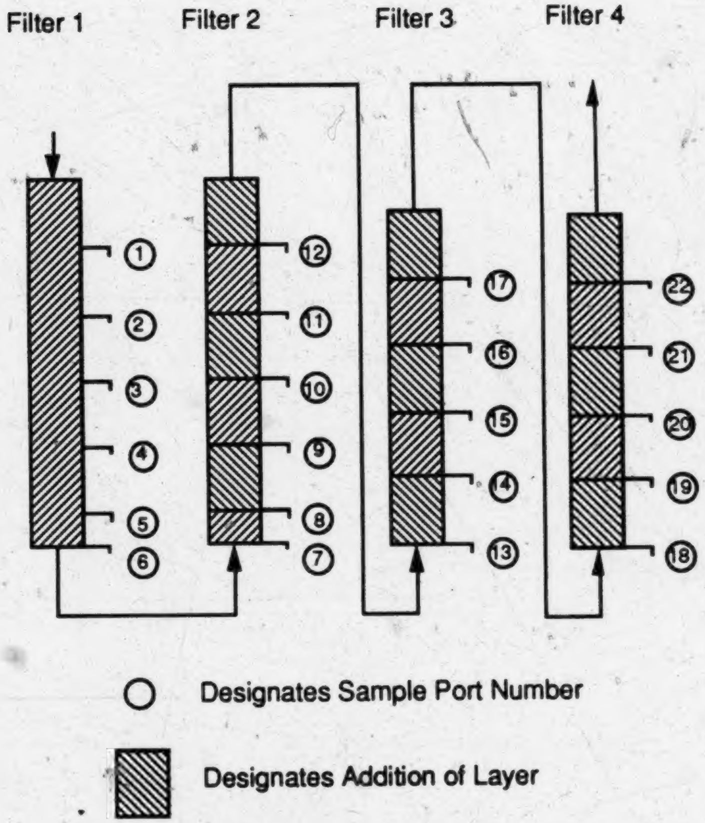


Figure 2.2 Capacity of a GAC Filter for Trichloroethylene as a Function of Filter Depth (Adapted from Baldauf, 1986)

trichloroethylene began to breakthrough. For this type of configuration, a throughput of 480 m^3 was treated to breakthrough. This was compared to a throughput of only 370 m^3 for the fixed bed reactor, representing an increase of 30% for the same total carbon bed height. The author reported that it was the stepwise addition of carbon, and not the upflow configuration itself, which led to the significant improvement in performance.

Further investigations concerning the stepwise operation of the same pilot scale GAC filter system are reported by Balduaf (1988). The investigation ultimately involved four GAC columns in series using the carbon Chemviron F-100®, all operated at a flow velocity of 10 m/h (Figure 2.3). The first column was operated as a fixed bed reactor in a downflow mode. Each time the effluent concentration of trichloroethylene reached 5% of the influent value, an additional 25-30 cm layer of GAC was added to the second (upflow) reactor. This procedure continued, with the creation of a third and ultimately a fourth reactor (both also upflow). The total investigation lasted 19 months and the columns were not backwashed during this time. Baldauf (1988) provides data showing that this mode of operation resulted in only a slight widening of the adsorption wavefront for trichloroethylene, in contrast to an extremely large widening of the DOC wavefront (i.e. the effect of fouling was minimized). Table 2.2 shows the loading obtained in the fixed bed adsorber vs that for the stepwise operated adsorber as a function of various trichloroethylene effluent concentrations. The loading for the stepwise adsorber is approximately twice as high and the comparison would be even more in its favor had the fixed bed


Filter 1
Filter 2
Filter 3
Filter 4
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
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⑭
⑮
⑯
⑰
⑱
⑲
⑳
㉑
㉒
○ Designates Sample Port Number
▨ Designates Addition of Layer

Figure 2.3 Schematic Diagram of Pilot Plant for Investigating Stepwise Addition of GAC (Adapted from Baldauf, 1988)

Table 2.2 Loading Obtained in a Fixed-Bed Adsorber vs a Stepwise Operated Adsorber (After Baldauf, 1988)

Trichloroethane Concentration (µg/L)	Solid Phase Loading (µg/g GAC)	
	Fixed Bed Height = 1.5 m	Stepwise Bed Height = 5.4 m
5	4.5	11.2
10	6.0	11.4
25	6.2	11.6

adsorber been operated with the same total bed height. In that case the average loading for the fixed bed adsorber would have been lower because of additional fouling.

Munz et al. (1988) have reported similar performance advantages associated with the stepwise bed system by conducting a direct comparison of layered upflow carbon adsorption (LUCA) to conventional fixed bed adsorbers. Results of this comparison are shown in Table 2.3. Based on throughput data, the LUCA configuration was shown to outperform a fixed bed upflow adsorber operated under similar conditions by a factor of 1.54. Therefore, for the same amount of activated carbon, 54% more water could be treated using this type of contactor operating procedure. The downflow bed exhibited a relative specific throughput which was 3% less than a similar upflow fixed bed (without the addition of layers). Overall, use of the LUCA mode of operation in this study resulted in a 40% increase in throughput when compared to an equivalent fixed bed adsorber with a depth of 1.85 m. This value is higher than the 30% increase reported by Baldauf (1986) for a partial application of the LUCA process in which only two GAC layers were applied following an initial fixed bed depth of 1.48 m.

Munz et al. (1990) reported that for adsorbers operated in an upflow mode, the reduction in capacity caused by pre-loading would be greater for more strongly, as opposed to weakly, adsorbing solutes since the strongly adsorbing solutes breakthrough slower, allowing more time for fouling to occur.

Fouling by high molecular weight natural organic matter will retard adsorption kinetics as well as reducing equilibrium capacity.

Table 2.3 Comparison of Throughput for Various GAC Contactor Operating Configurations (Bed Depth = 150 cm; Target Effluent Concentration = 5 μg/L Total VOCs; After Munz et al., 1990)

Adsorber Configuration	Hydraulic Loading (m/h)	EBCT (a) (min)	Time of Operation (days)	Specific Throughput L/mg GAC	Relative Specific (b) Throughput L/mg GAC
Upflow Fixed Bed	15.0	11.2	6.0	64.2	1.00
Layered Upflow Bed	15.0	11.4	6.0 (c)	98.8	1.54
Downflow Fixed Bed	10.0	11.6	9.0	62.4	0.97

(a) Empty bed contact time corresponding to a bed depth of 150 cm

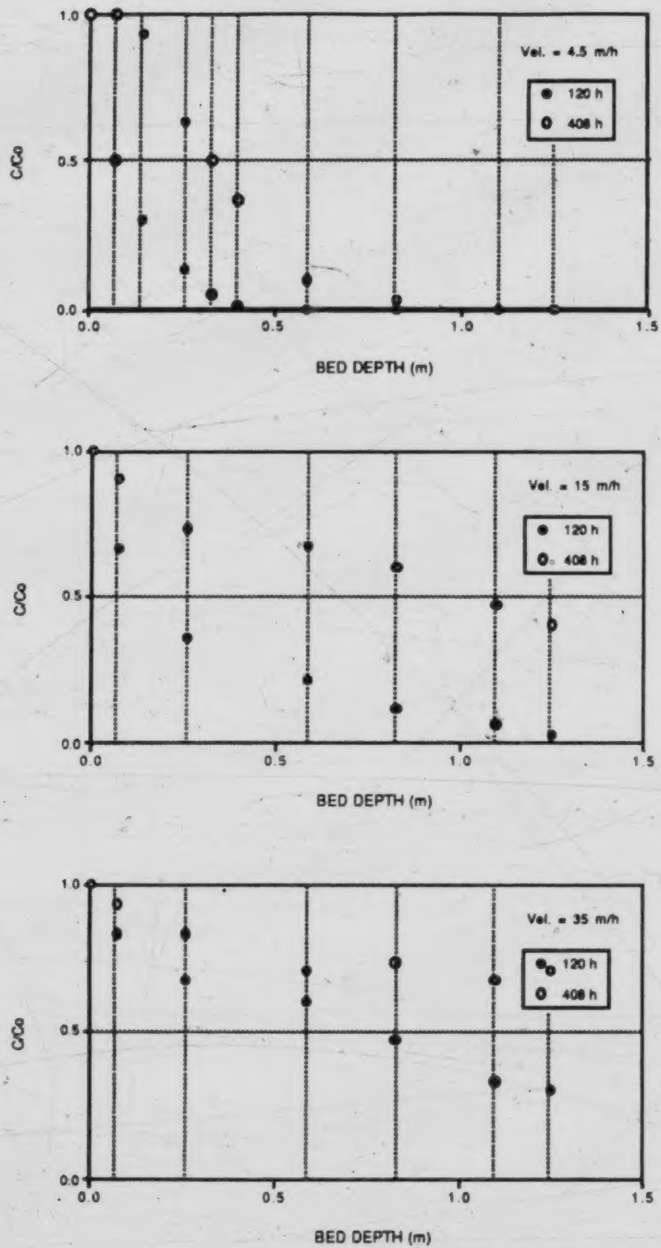
(b) Normalized values relative to Upflow Fixed Bed

(c) For Layered Upflow Bed, EBCT = 1.2 min. for each individual layer; for five layers cumulative EBCT = 6.0 min.

Zimmer (1988) has shown that fouling by DOC reduces the rate of internal (pore and surface) diffusion for a contaminant of interest, making the internal diffusion rather than film diffusion the rate-controlling mechanism. Surface diffusion is reduced sufficiently that pore diffusion becomes the controlling factor. The hindering effect of the humic substances on the reverse diffusion of small molecules suggests that concentration overshoots which are predicted for desorption of a weakly-adsorbing compound are not always observed in practice.

Some workers have proposed that the design of GAC contactors be based on scale-up methods which use data from mini-columns operated with smaller GAC particle sizes. Zimmer (1988) points out, as have Summers et al. (1988) and Speth and Miltner (1989), that these methods cannot be used successfully without a further understanding of the effect of particle size on fouling by background NOM. Summers et al. (1988) indicated that "fouling kinetics" are independent of particle size and suggest that some reaction or reorientation of the organic matter at the surface is rate-limiting. The effect of different filtration velocities on the breakthrough of a specific contaminant (1,1,1-trichloroethane) and DOC is shown in Figure 2.4. Slower velocities lead to a narrower mass transfer zones for both substances, while higher velocities can be used to hinder DOC adsorption (Figures 2.4e and 2.4f vs 2.4d). The compromise between these two considerations generally leads to operating velocities for adsorbers in the range of 10 to 15 m/h (Baldauf, 1987).

Zimmer (1988) suggests that in full scale GAC adsorbers, the



a

b

c

Figure 2.4 Effect of Filtration Velocities on Breakthrough of 1,1,1-Trichloroethane (a, b and c) and DOC (d, e and f) (Adapted from Baldauf, 1987)

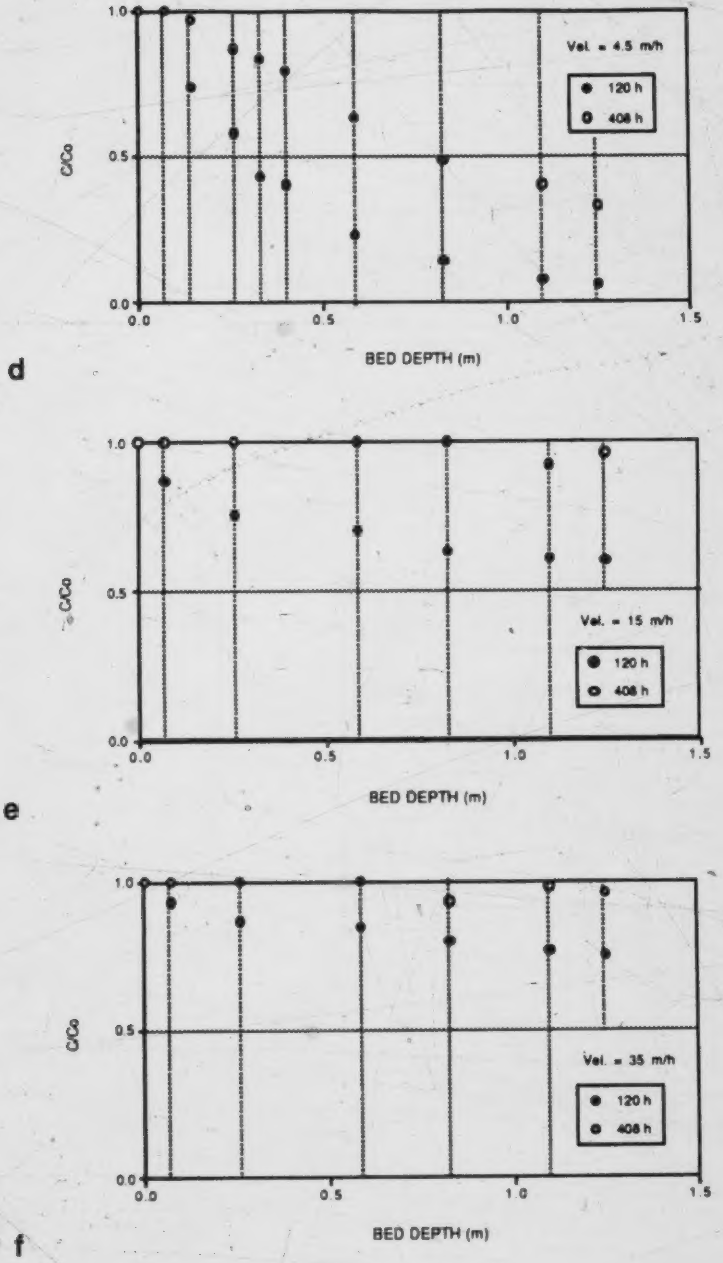


Figure 2.4 Continued

time to breakthrough for a specific parameter is more important than its equilibrium capacity. He evaluated the throughput of water treated as a function of empty bed contact time for various influent concentrations. Model calculations involving a mixture of trichloroethylene and tetrachloroethylene in a 3 to 1 concentration relationship, and a particular background DOC were generated. In each case, breakthrough of 10% of the initial concentration of trichloroethylene was taken as the endpoint. For low concentrations of trichloroethylene of less than 25 µg/L an empty bed contact time of 6 minutes was shown to be optimum. This optimum becomes less pronounced and shifts to an EBCT of 10 to 15 minutes as the influent concentration is increased. Figures 2.5a and 2.5b show the general effect of bed depth and filtration velocity, respectively, on throughput. At a filtration velocity of 10 m/h, a bed height of approximately 1.5 m is shown to be optimum, whereas at a bed height of 2 m, a velocity of approximately 15 m/h is optimum.

For conditions at Pforzheim, West Germany, Zimmer (1988) calculated that the use of two 1.5 m beds in series would give a 33% increase in the amount of water treated per unit weight of GAC (as compared to a single 3 m bed). He noted that this data confirmed the 31% increase in capacity for the same configuration as reported by Hörner and von Ehr (1985).

2.1.2 Implications of Pre-Loading Effects Due to NOM

The various studies reported indicate a considerable decrease in the effective capacity of GAC due to adsorption of NOM. For contactors operated in the downflow mode, this effect can be severe

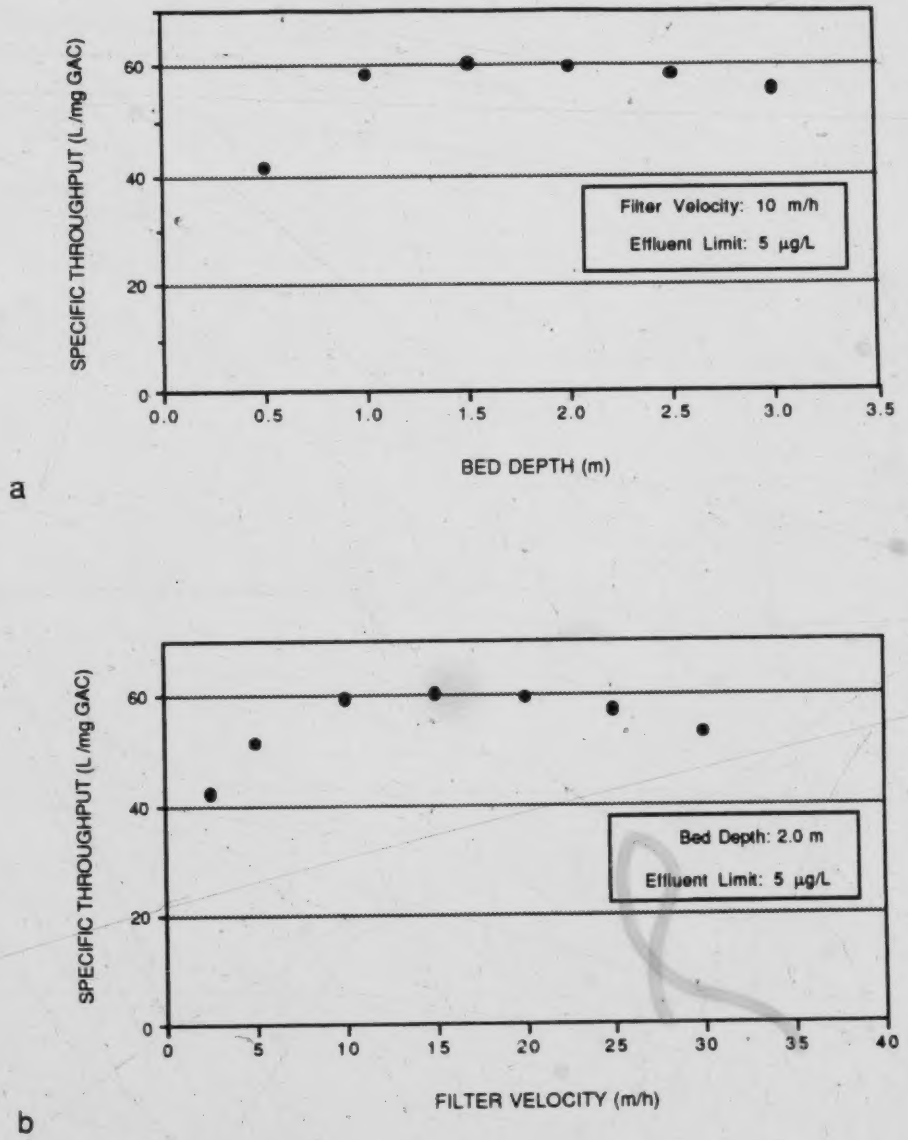


Figure 2.5 Effect of (a) Bed Depth and (b) Filtration Velocity on Throughput for Adsorption of a 50 μg/L Trichloroethylene, 17 μg/L Tetrachloroethylene Mixture (Adapted from Zimmer, 1988)

in middle and lower bed segments. The effect can however be minimized by the simple expedient of keeping as much as possible of the GAC from contacting the water until it is actually needed. This could be accomplished either by using shorter beds in series or by adding additional layers to an upflow bed. Other important aspects reported in the literature, concerning pre-loading can be summarized as follows:

1. The various investigations by Baldauf (1986, 1987, 1988), Baldauf and Zimmer (1986) and Zimmer et al. (1987a, 1987b, 1988) have been carried out using groundwater, whose natural organic matter is different that that for surface waters. However, a generally similar effect was reported by Summers et al. (1988) for a surface water. In addition a similar effect has been observed by Huck and Andrews (1988) in full scale GAC adsorbers treating a surface water. THM breakthrough profiles obtained in this study show almost no reduction in liquid phase concentrations in the lower two thirds of full-scale GAC contactors.
2. The impact of NOM on GAC capacity depends on the influent concentration and adsorbability of the contaminant of interest. For higher contaminant concentrations which would break through more quickly, a smaller beneficial effect would be expected by bringing the GAC into service incrementally, since there would be less time for fouling before the bed had to be taken out of service. Better adsorbing compounds will break through less quickly, therefore allowing more time for fouling and suggesting a greater advantage for an incremental

arrangement. Baldauf and Zimmer (1986) have shown that a weakly adsorbing compound (1,1,1-trichloroethene) reached approximately 50 to 62% of its single solute capacity as compared to a strongly adsorbing compound (tetrachloroethylene) which retained less that 10% of its original adsorptive capacity. The capacity reduction effect will also depend on the concentration and nature of the background NOM.

The results seen in these investigations are extremely significant for utilities contemplating the use of GAC. While ideally the effect of fouling could be minimized by the addition of relatively small layers of carbon as described by Baldauf (1988), this may not be practical. This mode of operation entails higher operating costs, and also requires frequent, if not continuous, monitoring of effluent concentrations. In addition, it offers reduced security, particularly in the case of changing influent concentrations.

There is an identified need for more information concerning the fouling of GAC by natural organic matter for surface water treatment conditions.

2.2 Application of Computer Models to Predicting GAC Adsorption of Organic Compounds

2.2.1 Competitive Adsorption (IAST)

Much of the predictive modelling considered in the literature has dealt with mixtures of known composition (Fritz and Schlünder, 1981; Fritz et al., 1981; Crittenden and Weber, 1978; Crittenden et al., 1980; Famularo et al., 1980). The capability of ideal adsorbed solution theory (IAST) to predict competitive interactions between chloroform, bromoform, thrichloroethene, tetrachloroethene, 1,2-dibromoethene and dibromochloromethane in various combinations of two, three and six solutes was evaluated by Crittenden et al. (1985b). This study represents one of the most comprehensive summaries of the application of IAST to known solutes.

A complete discussion of the details concerning the IAST model is presented elsewhere (Yen and Singer, 1984). IAST was originally developed to describe adsorption onto solids from a gas mixture (Gibbs, 1961) and later revised to address adsorption from liquids using single solute adsorption parameters. Yen and Singer (1984) reported that the model is very sensitive to single solute parameters used as input. Kong and DiGiano (1986) determined that the agreement between predicted and experimental results depends primarily upon the accuracy of experimental methods used to define single solute isotherm parameters.

There are five basic equations used in IAST to predict multicomponent behavior. As defined by Radke and Prausnitz (1972) and summarized by Crittenden et al. (1985b), these are:

$$q_T = \sum_{i=1}^{N} q_i \qquad i = 1, N \qquad (2\text{-}1)$$

$$z_i = q_i/q_T \qquad i = 1, N \qquad (2\text{-}2)$$

$$C_i = z_i C_i^o \qquad i = 1, N \qquad (2\text{-}3)$$

$$1/q_T = \sum_{j=1}^{N} z_i/q_i^o \qquad i = 1, N \qquad (2\text{-}4)$$

$$\frac{\pi_m A}{RT} = \int_0^{q_1^o} \frac{d\ln C_1^o}{d\ln q_1^o}\, dq_1^o = \frac{\pi_1^o A}{RT}$$

$$\int_0^{q_j^o} \frac{d\ln C_j^o}{d\ln q_j^o}\, dq_j^o = \frac{\pi_j^o A}{RT} \text{.......for } j = 2, N \qquad (2\text{-}5)$$

Equations 2-1 and 2-2 define the total surface loading where:

z_i = mole fraction of component i on the surface

q_i = surface loading for component i

q_T = total surface loading

N = number of components in mixture

Equation 2-3 is analagous to Raoult's Law where:

C_i^o = single solute liquid phase concentration in equilibrium with q_i^o

C_i = equilibrium liquid phase concentration

Equation 2-4 is an expression for zero area change upon mixing from the single-solute isotherms at the spreading pressure (surface tension) of the mixture where:

q_i^o = single solute solid phase concentration for component i, evaluated at the spreading pressure of the mixture

Equation 2-5 relates the spreading pressures of the pure compound systems to the spreading pressure of the mixture where:

π_m = spreading pressure of the mixture
A = specific surface area of the adsorbent
R = ideal gas law constant
T = absolute temperature
π_i^o, π_j^o = spreading pressure of single solute components i,j

If the Freundlich isotherm equation is used to describe single solute behavior in Equation 2-5, a new equation may be derived for calculating C_i as follows:

$$C_i = z_i \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} \qquad i = 1, N \qquad (2\text{-}6)$$

Where: n_i = inverse of the Freundlich parameter 1/n for component i
K_i = Freundlich capacity parameter K for component i

Equation 2-6 may then be combined with the equilibrium mass balance equation (2-1) such that the liquid phase concentration (C_i) may be eliminated. IAST predictions for bottle point isotherms then, only require that the single solute isotherm parameters and initial concentrations be known for each component and that values for bottle volume and carbon dosage be specified.

To allow quantitative comparisons between experimental data and IAST predictions, use of two different equations has been reported by Kong and DiGiano (1986) and Crittenden et al. (1985b). The equation (2-7) proposed by Kong and DiGiano (1986) provides an indication of the goodness of fit by calculating the sum of squares of errors in the liquid phase concentration data.

$$SSE = \sum (C_i - \hat{C}_i)^2 \qquad (2\text{-}7)$$

Where:

SSE = sum of squares of errors
C_i = observed concentration of component i at equilibrium
$\hat{C}_i$ = predicted concentration of component i at equilibrium

The authors report that there were notable differences between predicted and observed data at low adsorbent dosages (high liquid phase concentrations) however no error data were presented. An alternative equation (2-8) has been presented by Crittenden et al. (1985b) which evaluates data agreement in terms of an average percentage error (APE).

$$APE = \frac{100}{N} \sum \frac{| X_{observed} - X_{predicted} |}{X_{observed}} \qquad (2\text{-}8)$$

Where:

APE = average percentage error
$X_{observed}$ = observed liquid or solid phase concentration at equilibrium
$X_{predicted}$ = predicted liquid or solid phase concentration at equilibrium
N = number of data points

Use of this equation allows APEs to be calculated for both liquid and solid phase equilibrium data. Division by the observed (experimental) value normalizes the error and allows APEs for compounds of widely varying adsorptive strengths to be directly compared. Such a direct comparison could not be obtained using the residual sum of squares approach. From an interpretation of APEs Luft (1984) has shown that IAST predictions were as precise as the experimental methods used to determine single solute isotherm data. He reports for example, that APEs for trichloroethane were 14% and 1.5% in C_i and q_i respectively for single solute isotherm data, increasing to 22% and 4% respectively for a six component mixture. Typical APE data obtained from IAST predictions for two, three and six component mixtures using Filtrasorb 400® carbon are shown in Table 2.4 (Crittenden et al., 1985b). Overall, APEs of 29% and 16% for C_i and q_i, respectively, were reported by Crittenden et al., (1985b) for 256 multicomponent isotherm data points. Using the same type of error analysis, Jossens et al. (1978) reported that for two component mixtures involving phenolic compounds, the APE in q_i ranged from 3% to 22%. No APEs were reported for C_i. The same authors proposed that systematic deviations between calculated and observed results may be attributed to acidities of the solutes and suggested that adsorption experiments be conducted under controlled pH conditions to minimize this effect.

2.2.2 Other Multicomponent Models

DiGiano et al. (1978, 1980) developed a simplified model for the prediction of competitive adsorption equilibria based on the

Table 2.4 Typical APE Data Obtained From IAST Predictions (After Crittenden et al., 1985b)

Mixture	Components (a)	Initial Concentration In Mixture	Relative % Error Using IAST		Number of Data Points	C Range (μM/L)	q Range (μM/g)
			C	q			
1	Chloroform	10.9	8	20	16	2.53-10.3	13.6-53.0
	Trichloroethene	70.4	84	18		0.512-56.9	113-1151
2	Chloroform	38.5	22	30	23	4.16-37.4	15.7-82.1
	Trichloroethene	35.4	24	2		0.102-30.6	16.2-389
	Bromoform	30.2	27	15		0.198-27.0	13.8-256
3 (b)	Chloroform	14.0	64	21	22	0.05-14.0	1.7-66
	Trichloroethene	13.5	22	4	24	0.04-12.3	7.4-224
	Dibromochloromethane	12.4	24	13	24	0.13-11.9	6.7-128
	1,2-dibromomethane	13.4	22	8	24	0.13-12.7	7.3-146
	Bromoform	11.4	19	12	23	0.07-10.9	6.5-195
	Tetrachloroethene	12.3	45	4	14	0.04-5.4	95.7-915

(a) Using Filtrasorb 400® Carbon

(b) Temperature 10-12 °C, all others 20-22 °C same concepts as IAST. The simplified competitive adsorption model (SCAM) presented by the authors was based on one initially proposed by Baldauf et al. (1977) and extended by Frick (1977) to enable straightforward calculations of competitive adsorption for any number of components. The simplified model was shown to provide good agreement with IAST in the concentration range typically expected in water treatment (0.01 to 0.1 mmol/L). Disadvantages associated with the use of SCAM, including limitations over broad concentration ranges, are described by Weber and Smith (1987).

2.2.3 Competitive Adsorption in Unknown Mixtures

Prediction of the removal of organic compounds in unknown mixtures, for example, in drinking water containing many competing solutes is reported by Frick and Sontheimer (1983), Crittenden et al. (1984a) and Luft (1984). The technique used involves combining the competitive effect of the background organics into "fictive", "theoretical", "pseudo" or "hypothetical" (HC) components, the adsorptive properties of which can be obtained without prior knowledge of the unknown background competition. A similar approach concerning grouping of the unknown components has been reported by Caligaris and Tien (1982). In the study reported by Crittenden et al. (1985c) the HC parameters (Freundlich K and 1/n, and initial concentration C_{io}) were determined by measuring the adsorption of a weakly adsorbing tracer compound which was either added to the background mixture or already present. The HC parameters are generated by fitting the liquid and solid phase isotherm data for the tracer component in the mixture such that the average percentage error is minimized. The parameter search routine used to calculate the HCs has been described by Speth (1986).

Sontheimer et al. (1988) suggest that in order to apply the use of hypothetical or "fictive" components in adsorption analysis, the multicomponent model applied should address the following criteria:

1) The model should be simple to use and satisfy IAST,
2) The model must describe DOC isotherm data in addition to known single substances in the unknown multicomponent mixture,
3) The HC parameters must provide results which may be used to directly understand the influence of a water treatment process,
4) Results obtained for a specific water and activated carbon should be readily transferrable to other carbon types.

Use of the IAST model in conjunction with the Freundlich equation is recommended due to its simplicity and the ability of adjustable parameters to compensate for errors (Sontheimer et al., 1988).

Crittenden et al. (1984a, 1985c) reported that the use of HCs in conjunction with IAST, allowed competitive isotherm data to be predicted for six individual VOCs in an actual groundwater. The degree of fit of predicted to experimental data was assessed using

APEs. In all cases the concentrations of organic compounds of interest were increased by spiking to approximately 8 μmol/L prior to conducting multicomponent isotherms. No isotherm analyses were reported for the actual contaminant concentrations which ranged from 21 to 213 μg/L. Wang and DiGiano (1988) attempted to use IAST with HCs to describe competitive interactions of five synthetic organic chemicals (SOCs) in the presence of ozonated and unozonated humic substances. The predicted isotherm for each SOC however was in poor agreement with experimental data. The authors attributed this problem to wide differences in the TOC attributable to the humic substance background and individual SOCs, which interfered with the minimization of error in obtaining HCs.

Total organic halogen (TOX) data may also be predicted by the use of HCs. Crittenden et al. (1985c) have shown that TOX competitive isotherm data may be predicted using two HCs which were fit to a dibromochloromethane tracer component.

Volker et al. (1982, 1984) have developed a method which allows fictive components based on a reference carbon, to be related to other carbons. Initially, both fictive components and DOC isotherm parameters are defined for the reference carbon. The K values for fictive components relating to other carbons may then be determined by using a correlation between single solute K values for a specified compound on both the reference carbon and other carbons.

2.2.4 Mulitcomponent Fixed Bed Models

In this section, the most commonly used adsorption models which describe breakthrough in GAC contactors are described, and for illustrative purposes, predicted data are compared. The equilibrium column model (ECM) will be discussed first, since this is the only model which allows fixed bed breakthrough to be predicted, assuming no mass transfer resistance.

The ECM proposed by De Vault (1943) was developed to predict adsorption column performance for step-up influent concentrations and plug flow conditions, in the absence of mass transfer resistance. IAST is used to describe competitive adsorption equilibrium in multicomponent mixtures. The ECM arbitrarily divides a GAC bed into zones. Each zone contains a fraction of each of the solutes, the length of which is dependent upon their relative adsorbability. As shown in Figure 2.6, the total liquid phase concentration is assumed to be the sum of the individual components (Sontheimer et al., 1988). To assist in explaining the ECM, Sontheimer et al. (1988) suggest numbering the zones such that zone k defines the zone located at the front of the bed, containing k adsorbable components. An interface between two zones is called a front. Zone k completely contains the most strongly adsorbing component, component k. As a result of competitive interactions encountered in zone k, component k-1 will be present in both zones k and k-1. Component k-2 will be present in zones k, k-1 and k-2 since it is more weakly adsorbed than either component k or k-1.

As the influent proportion of the bed (zone k) becomes saturated by the strongest adsorbing component, it causes weaker adsorbing components to be displaced downward at concentrations higher than those measured in the influent. This displacement process continues until the most weakly adsorbing component enters

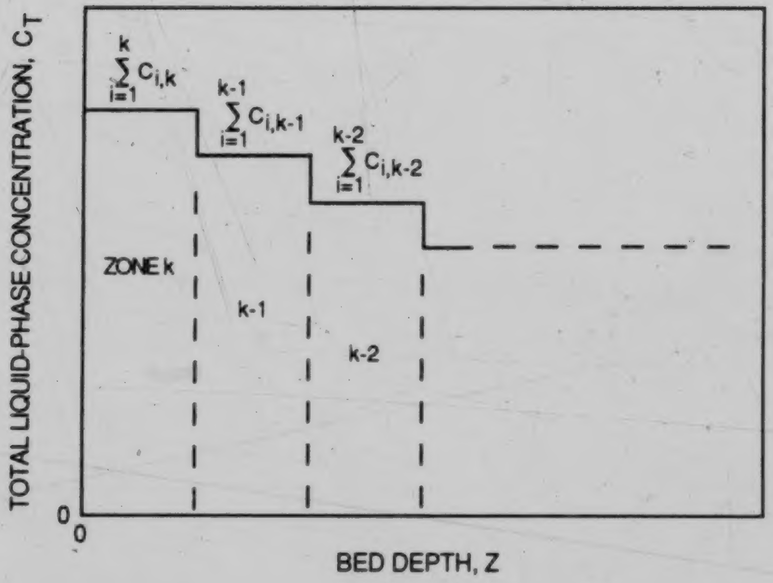

TOTAL LIQUID-PHASE CONCENTRATION, C_T
$\sum_{i=1}^{k} C_{i,k}$
$\sum_{i=1}^{k-1} C_{i,k-1}$
$\sum_{i=1}^{k-2} C_{i,k-2}$
ZONE k
k-1
k-2
0
0
BED DEPTH, Z

Figure 2.6 Representation of Zones Present in a GAC Bed as Described by the ECM (Adapted from Sontheimer et al., 1988)

the bottom zone in the column , at a concentration higher than in any previous zone.

Appropriate mass balance equations have been derived which allow the velocity of the fronts and the concentration in each zone to be described (Luft, 1984; Crittenden, et al., 1987). Equation 2-9 describes the concentration of component i in zone k.

$$C_{i,k} = \frac{(q_{i,k} - q_{i,k-1})\, \rho_B\, Vw_{k-1}}{(V_f - Vw_{k-1})\, \varepsilon} + C_{i,k-1} \tag{2-9}$$

Where:

$C_{i,k-1}$ = liquid-phase concentration component i, zone k-1

$q_{i,k-1}$ = solid-phase concentration component i, zone k-1

ρ_B = bulk density

Vw_{k-1} = velocity of wave front between zones k-1 and k

V_f = interstitial fluid velocity

ε = bed void fraction

This equation is also used to calculate the highest effluent (overshoot) concentration due to competitive adsorption for each component.

Equation 2-10 is used to determine the wave velocity (Vw_k) using a mass balance over the entire bed, as zone k breaks through. The amount of solute present in zones 1 through k is equated to the amount of solute fed.

$$Vw_k = \frac{V_f \varepsilon C_{0k} - \sum_{j=1}^{k-1}[(q_{k,j}\, \rho_B + C_{k,j}\, \varepsilon)(Vw_j - Vw_{j-1})] + (q_{k,k}\, \rho_B + C_{k,k}\, \varepsilon) Vw_{k-1}}{(q_{k,k}\, \rho_B + C_{k,k}\, \varepsilon)} \tag{2-10}$$

Where:

C_{0k} = influent concentration of component k

Vw_{j-1} = 0 for j=1; Equation 2-10 is valid for $k \geq 2$

Equations 2-9 and 2-10 may be used in conjunction with IAST to predict for each zone in the bed: 1) bed volumes fed to breakthrough, and 2) velocity of the center of mass for each wave front. The IAST Equation 2-11 (Crittenden et al., 1987) is a simplification of ideal adsorbed solution theory equations developed by Fritz et al. (1981) and Crittenden et al. (1985b) which use the Freundlich adsorption equation.

$$C_{i,k} = \frac{(q_{i,k})}{\sum_{j=k}^{N}(q_{j,k})}\left[\frac{\sum_{j=k}^{N}(n_j q_{j,k})}{n_i K_i}\right]^{n_i} \quad (i=1,N) \qquad (2\text{-}11)$$

Where:

n_i = reciprocal of the slope of the Freundlich isotherm

K_i = Freundlich capacity parameter

In addition, the ECM is capable of predicting for each component; 1) concentration in individual zones, 2) average surface loading, and 3) GAC treatment capacity. Detailed information regarding these calculations is presented in Section 5.8.2.

Crittenden et al. (1987) compared breakthrough of a weakly adsorbing SOC (cis-1,2-dichloroethene (DCE)), predicted using the

ECM, to pilot column data collected at six different empty bed contact times (EBCTs). Based on visual observations the ECM approximately predicted the midpoint of breakthrough, and the highest overshoot concentration. Also shown was the improved ability of the ECM to predict breakthrough behavior as the EBCT increased, resulting from a decrease in the length of the mass transfer zone (MTZ). Similar results are reported by Hand et al. (1989) for pilot scale EBCTs using columns placed in series. Crittenden et al. (1985b) report that the ECM will provide an approximate prediction of the effluent concentration in cases where the bed length is greater than three to four times the depth of the MTZ. For more strongly adsorbing solutes (trichloroethene and tetrachloroethene), predictions using the ECM was less accurate because mass transfer exhibited a greater impact on breakthrough profiles. The use of HCs to represent background competition or capacity reduction due to fouling, however, were not evaluated. HCs were used in ECM predictions conducted by Vaith et al. (1988). Predictions using five HCs were found to underestimate breakthrough for a pilot column having an EBCT of 15 minutes. ECM predictions were found useful in estimating GAC usage rates when compared to using single solute calculations evaluated at several influent concentrations, since the ECM considers competitive interactions. Crittenden et al. (1987) report that use of the ECM is preferable to using raw isotherm results for prediction of carbon usage. In isotherm bottles, all components compete for adsorption sites, whereas in a fixed bed, strongly adsorbed components are removed at the beginning and do not exhibit the same competitive effect with respect to more weakly adsorbing components which are adsorbed at lower depths.

Crittenden et al. (1987) have shown that the number of components used as spiked compounds in pilot studies can be reduced through appropriate use of the ECM. Selection of one compound to represent competition attributable to a group of similar compounds is possible by adjusting the influent concentration of the chosen compound such that breakthrough predictions for the other compounds of interest remain unchanged. The number of components required to be described in mass transfer input data may also be reduced, by utilizing ECM overshoot concentrations as influent concentrations (Crittenden et al., 1985a; Crittenden et al., 1988; Sontheimer et al., 1988). Friedman (1984) reports that this method can be used in cases where the mass transfer zone does not allow spreading of strongly adsorbing compounds, causing them to compete with weakly adsorbing compounds.

2.2.5 Mass Transfer Models

Two of the most commonly used models which incorporate mass transfer parameters are the pore surface diffusion model (PSDM) and the homogeneous surface diffusion model (HSDM) (Sontheimer et al., 1988; Crittenden et al., 1987; Hand et al., 1989, 1984, 1983; Kuennen et al., 1989, 1988). The fundamental basis of earlier modelling work incorporating mass transfer parameters is presented by Crittenden et al. (1980). Typically, the PSDM and HSDM models can be used to predict fixed bed adsorber dynamics in both known and unknown background mixtures.

The PSDM incorporates the following assumptions, as reported by Kuennen et al. (1988):

1) Intraparticle transport described by both pore and surface diffusion,
2) Film transfer resistance accounted for at the GAC surface,
3) Local adsorption equilibria at the GAC surface as defined by Freundlich isotherm parameters,
4) Multicomponent equilibria at the GAC surface as described by IAST,
5) Advection dominates axial transport in a fixed bed adsorber.

Mechanisms incorporated by the HSDM are similar except that pore diffusion is neglected. Detailed methods describing the determination of mass transfer parameters required as input to the PSDM and HSDM models have been described elsewhere (Hand et al., 1984, 1983). User-oriented solutions to the HSDM developed by Hand et al. (1983) may be used to :

1) Plan the scope of pilot plant studies,
2) Interpret pilot scale test results,
3) Investigate mulitstage adsorber configurations,
4) Estimate preliminary costs for fixed bed asdsorbers.

Recent attention has been focused on evaluating GAC use rate as a function of EBCT and in the presence of NOM (Zimmer et al., 1988; Hand et al., 1989). As described by Zimmer et al. (1987a), heterogeneous humic substances compete with trace organics for limited adsorption sites. This effect can be represented as a reduction in the Freundlich K by conducting isotherms using carbon which has been pre-loaded for various periods of time. To represent this reduction in the HSDM, assuming that surface diffusion dominates, Zimmer et al. (1987a) recommend replacing the Freundlich single solute capacity parameter (K), by a time-dependent one (K(t)). Sontheimer et al. (1988) proposed an equation (2-12) which describes the decrease in Freundlich K, as having an initially rapid (exponential) decrease, followed by a linear decrease representing a long term slow decrease.

$$K(t) = K_0\,[K_1 - K_2 t + K_3 \exp(-K_4 t)] \qquad (2\text{-}12)$$

Where:

$K(t)$ = Freundlich capacity at time, t

K_0 = initial Freundlich capacity

$K_{1,2,3,4}$ = Freundlich capacity at time, $t_{1,2,3,4}$

Zimmer et al. (1987b) present data which demonstrates the successful simulation of breakthrough by including the following assumptions in the HSDM:

1) The influence of NOM is accounted for by a time-dependent capacity term,
2) Small competitive interactions between compounds are taken into consideration using IAST,
3) A reduction in the internal surface diffusion of approximately one order of magnitude occurs as compared to humic-free adsorption.

In later studies by Zimmer et al. (1988), the PSDM was used with both a time-variable K (PSDM-K(t)) and tortuosity value to predict breakthrough of trichloroethene and tetrachloroethene in actual full scale adsorbers. The presence of NOM was shown to eliminate surface diffusion. PSDM-K(t) predictions for single adsorbers with an EBCT of 9 to 15 minutes yielded the largest specific throughputs; two adsorbers operated in series with similar EBCTs were reported to treat approximately 35% more water than a single adsorber.

Hand et al. (1989) compared PSDM predictions to pilot scale breakthrough data [illegible] [illegible]chloroethene and trichloroethene at various EBCTs. An increase of 40 to 50% in throughput was realized for a beds-in-series as compared with a single adsorber type of operation. These results are consistent with those reported by Zimmer et al. (1988). Additional investigations conducted by Hand et al. (1989) have shown that as NOM pre-loading time increases, the pore diffusion flux contribution to intraparticle mass transfer exceeds the surface diffusion mechanism. For PSDM calculations, surface diffusivities were set to zero and pore diffusivities were calculated from liquid diffusivities by adjusting the tortuosity until the model predictions approximated pilot scale breakthrough data. Therefore the PSDM calculations considered only the effect of NOM on reducing kinetics, capacity reduction was not included. Hand et al. (1989) suggests that further development of methods for obtaining fixed bed model parameters is required to accurately predict breakthrough of synthetic organic compounds in the presence of NOM. Fettig and Sontheimer (1987 a, b, c) present information concerning the kinetics of adsorption for single and multicomponent systems in the presence of DOC.

Summers et al. (1989) have summarized previous modelling approaches reported by Zimmer et al. (1988) and Sontheimer et al. (1988) concerning the use of pre-loaded isotherm data with either the HSDM or PSDM. The authors propose an alternative approach which involves first pre-loading small GAC particles and then performing a small-scale column test. Breakthrough of trichloroethene in full-scale beds, however, was not well predicted using this approach because of long-term reductions in adsorption capacity. Speth and Miltner (1989) agree that a better knowledge of NOM pre-loading is required prior to a scale-up type of procedure being accepted.

Munz et al. (1990, 1988) evaluated the use of the HSDM in predicting the performance of a layered upflow carbon adsorber (LUCA) configuration. Munz and Boller (1989) made similar comparisons except using the PSDM. Breakthrough curves modelled with the HSDM assumed constant capacity (K) and surface diffusion (D_S) (Munz et al., 1988). The effect of these parameters on model predictions was noted as follows; D_S determines the steepness of the breakthrough curve (length of the MTZ) whereas K determines the position of the breakthrough curve with respect to time. A good fit of predicted data to that obseved in pilot studies was observed when the LUCA adsorber was modelled as a fixed bed reactor of variable bed depth or EBCT. This method of operation was therefore modelled as N fixed bed adsorbers in series.

Use of the PSDM, assuming constant values for K and D_S

resulted in breakthrough being underestimated by approximately 5 to 15% when compared to pilot plant data. The authors, however, cite the work of Summers et al. (1989) and Hand et al. (1989) noting that the equilibrium capacity and kinetics of initial GAC layers could be slowly reduced by fouling with DOC and suggest that a better mechanistic understanding is required prior to establishing generalized conclusions.

2.3 Removal of Chlorination By-Products Using GAC

2.3.1 Haloforms

Rook (1976) investigated conditions for haloform formation and discussed the application of experimental data to practical water treatment. A mixture of CH_2Cl_2, CCl_4, $CHCl_3$, and $CHBr_3$ was continuously fed into identical 3 m deep GAC columns at various contact times. Concentrations of individual compounds were in the range of 2-4 mg/L. For a 12 minute contact time, breakthrough occurred after 22 days for $CHBr_3$; after fourteen days for CCl_4; after seven days for $CHCl_3$; and after two days for CH_2Cl_2.

In a report on pilot scale studies, Yohe et al. (1981) noted that chloroform comprised 79 to 94 percent of the instantaneous TTHM measured at a Philadelphia water treatment plant. Sharp breakthrough of chloroform and chloroform precursors were noted immediately following start-up in GAC columns of 1 m bed depth. Influent chloroform levels ranged from 71 to 176 µg/L, averaging 102 µg/L over the 14 week study period. Exhaustion was not observed to occur until approximately 9 weeks after start-up.

Cumulative mass loadings displayed a levelling trend as exhaustion was approached (Yohe et al., 1981; Cairo et al. 1979). In similar studies by Wood and DeMarco (1979) a continuous low level passage of chloroform was noted prior to major breakthrough at 28 days. This study utilized 1.5 m carbon bed depths and a contact time of 12.5 minutes.

In pilot scale studies (USEPA, 1980) breakthrough and exhaustion for bromodichloromethane occurred after 15 and 45 days respectively. Similar points for chloroform were reached after 8 and 23 days.

Cairo et al. (1979) evaluated the performance of carbon on the basis of mass loadings. Comparing different modes of operation, chloroform removal was 20% higher in a contactor than in a filter adsorber (where existing sand filters were modified to accept GAC media). The carbon in both columns was Filtrasorb 300®. In the same study, a carbon with smaller grain size (Filtrasorb 400®) was found to be more effective in removing chloroform than a larger carbon (Filtrasorb 300®) when both were operated in a similar contactor mode. Forsyth et al. (1982) reviewed chloroform cumulative mass loadings and found that loadings in the range of 0.42 to 1.6 mg/g of GAC would be expected at column exhaustion.

Summers and Roberts (1983) compared the breakthrough of TOC, TOX and 20 specific organic compounds using fresh, once-regenerated, and exhausted Filtrasorb 300® GAC. The authors suggest that competitive adsorption may have been the underlying cause of effluent chloroform conentrations which greatly exeeded influent concentrations during relatively stable influent concentrations of approximately 15 µg/L. The adsorptive capacity of fresh and regenerated GAC for chloroform was reported as 0.072 mg/g and 0.058 mg/g respectively, measured at the maximum cummulative mass removed. The authors suggest that an observed net production of chloroform in the contactors may have been the result of a reaction between organic precursor material and residual chlorine.

An examination of mass loading with respect to depth was presented by the USEPA (1980). Expressed on a per gram of GAC basis chloroform loadings increased with depth, whereas bromodichloromethane loadings did not appear to change significantly. Average chloroform and bromodichloromethane influent concentrations were 67 µg/L and 47 µg/L respectively.

Gammie and Giesbrecht (1986b, 1987) report that for total trihalomethane (TTHM) influent concentrations ranging from 40 µg/L to 70 µg/L, breakthrough of low concentrations occurred in 3.05 m GAC contactors within a few days of start-up. A very broad wavefront was observed which slowly extended over the entire bed depth. Based on liquid phase concentration data, the top 0.6 m of the 3.05 m bed depth attained the highest loading of 1.4 mg/g of GAC. Reported loadings were greatly reduced in mid to lower bed depths with an overall loading of only 0.6 mg/g. Similar results were reported for pilot scale studies using various carbons by Andrews (1987).

2.3.2 Mutagenic Compounds

This section reviews results of recent studies on the mutagenicity of drinking water, and describes the relevance of the mutagenic compound MX to drinking water treatment. The effectiveness of GAC for removing mutagenicity, and specifically MX from water is addressed.

2.3.2.1 Mutagenicity of Drinking Water

A considerable amount of literature is available which shows that finished drinking water can display mutagenic activity (Loper, 1980; Nestmann, 1983; Meier and Bull, 1985; Hemming et al., 1986). Most organic compounds present in drinking water are formed in very low concentrations (Lucas, 1985; Hemming et al., 1986; Meier et al., 1986) and little is known concerning their mutagenic activity (Bull, 1982; Haworth et al., 1983; Mortelmans et al., 1986). A recent review concerning drinking water mutagenicity is provided by Noot et al. (1989).

Disinfection by-products constitute a large fraction of the compounds which have been identified as contributing to mutagenicity (Maruoka and Yamanaka, 1980; Cheh et al., 1980, de Greef et al., 1980). Some of these result from the disinfection of aqueous solutions which contain natural humic material (Meier et al., 1983; Coleman et al., 1984; Kopfler et al., 1985; Meier et al., 1986). These compounds include halogenated and non-halogenated nitriles, ketones, acids, aromatic compounds and aldehydes. Kopfler et al. (1985) and Meier et al. (1986) reported that some of these compounds are known mutagens while most have yet to be tested.

Fielding and Horth (1986) and Horth et al. (1987) studied the production of mutagenic compounds by the reaction of chlorine with amino acids. These results were then compared with by-products obtained using humic substances. Mutagenic activity which was similar to that produced during drinking water chlorination was generated by laboratory chlorination of humic and amino acids (Fielding and Horth, 1986).

Studies conducted by Meier et al. (1986) and Fielding and Horth (1986) showed that only a small fraction of the observed mutagenicity in drinking water could be related to specific compounds. For example, Table 2.5 shows that the total expected mutagenic activity arising from compounds identified in a chlorinated humic acid sample accounted for less than 7% of the observed activity. This situation has changed, however, with the detection of the compound MX in drinking water, as discussed in the next section.

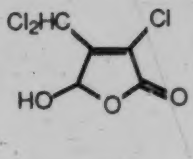
2.3.2.2 Relevance of MX to Drinking Water

The compound known as MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] (Figure 2.7) may be responsible for 5-20% of the mutagenicity observed in drinking water (Hemming et al., 1986). In other studies up to 57% of the acid fraction mutagenicity seen in some drinking water samples could be attributed to MX (Kronberg and Christman, 1988; Hemming et al., 1986; Meier et al., 1987; Kronberg et al., 1985; Kronberg et al., 1988). Research conducted by Holmbom et al. (1984) identified MX as a potent mutagen in spent pulp mill bleaching liquors. The abbreviated name

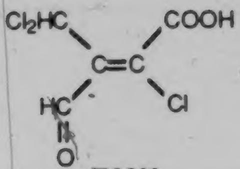
Table 2.5 Contribution of Identified Mutagenic Compounds to the Total Mutagenicity of a Chlorinated Humic Acid Sample (After Meier et al., 1986)

Compound	Concentration	Specific Activity TA100 Net Revertants	Theoretical Contribution to Mutagenicity Net Revertants	Total Percentage
	mg/L	/mg	/mL	%
Dichloroacetonitrile	5.3	645	3.42	0.13
1,1-Dichloropropanone	1	38	0.04	<0.01
1,3-Dichloropropanone	0.15	113,900	17.08	0.67
1,1,1-Trichloropropanone	9.8	753	7.38	0.29
1,1,3-Trichloropropanone	0.05	24,633	1.23	0.05
1,1,3,3,-Tetrachloropropanone	2.6	7,790	20.31	0.80
Pentachloropropanone	7.2	3,710	26.71	1.05
3,3-Dichloropropenal	0.06	5,830	0.35	0.01
2,3,3-Trichloropropenal	0.035	2,560,000	84.6	3.53
Sum of Identified Compound			166.12	6.55
Total Sample Activity (a)			2537±196	(100.00)

(a) Mean slope value ± Standard deviation of the mean


Cl₂HC
Cl
HO
O
O

MX


Cl₂HC
COOH
C=C
HC
Cl
O

EMX

(MX) 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone

(EMX) 2-chloro-3-(dichloromethyl)-4-oxo-butenoic acid

Figure 2.7 Structures of MX and EMX

"MX" represents "Mutagen X" as it was designated prior to structure elucidation.

Kringstad (1985) and Coleman et al. (1984) observed that pulp mill chlorination by-products were similar to those produced using humic substances. Ertel et al. (1984) linked humic material to lignin which has been identified as a major component of wood. Many authors have reported the presence of MX in chlorinated humic acid extracts (Meier et al., 1986; Hemming et al., 1986; Meier et al., 1987, Kronberg et al., 1986; Kronberg et al., 1988; Holmbom et al., 1987; Backlund et al., 1988). As well, MX has been identified in drinking water by Hemming et al. (1986), Meier et al. (1986), Kronberg et al. (1985, 1986, 1988) and Holmbom et al. (1987).

Hemming et al. (1986) showed that concentrations of MX producing mutagenicity in a chlorinated lake humic water were in the range of 280 to 510 ng/L. Fielding and Horth (1986) reported that as little as 2 to 10 ng/L (0.002 to 0.010 µg/L) would account for the TA100 mutagenicity in XAD/diethyl ether extracts which they observed in water sampled after chlorination.

Meier et al. (1987) and Holmbom et al. (1987) investigated the stability of MX in aqueous solution as a function of pH and temperature. Meier et al. (1987) reported that at 23°C the order of persistence of MX activity, as related to pH was pH 2 > pH 4 > pH 8 > pH 6. The authors also reported that the loss of mutagenic activity occurred exponentially with respect to time, indicating first order kinetics. Based on mutagenicity decay curves, the half-life at pH 6 and 23°C was reported as 2.3 days.

Many authors (Kronberg and Christman, 1988; Horth et al., 1987; Kronberg et al., 1985; Kronberg et al., 1988) have reported that one of the degradation products is an open ring isomer in the "E" configuration [E-2-chloro-3-(dichloromethyl)-4-oxo-butenoic acid] (Figure 2.7). This compound, referred to as "EMX" has been shown to exhibit approximately 10 times less mutagenicity than MX (Kronberg et al., 1988). Kronberg et al. (1987) have shown for conditions of low pH and elevated temperatures, that EMX is capable of slowly converting back to MX. Therefore, from a health perspective, the authors state that there should not be a significant increase in mutagenicity of consumed water, despite the highly acidic conditions present in the alimentary canal. Kronberg (1987) and Kronberg and Christman (1988) identified the MX analogs 3-chloro-[illegible]-(dichloromethyl)-2(5H)-furanone (red-MX) and 2-chloro-3-(dichloromethyl)-2-butendioic acid (ox-MX) in chlorinated water samples, but reported that the mutagenicity associated with these compounds would be very weak in comparison to MX.

Studies conducted in the United States (Meier et al., 1987) and Finland (Hemming et al., 1986; Kronberg and Vartiainen, 1987) evaluating a total of thirty different localities with total organic carbon (TOC) concentrations of up to 20 mg/L reported MX concentrations ranging from 1 to 194 ng/L. Coleman et al. (1987) found that for three United States drinking waters sampled, the highest MX concentration obtained also corresponded to the highest TOC concentration. To date however, there are no published results concerning the removal of MX or EMX in water treatment processes.

Holmbom et al. (1987) and Backlund et al. (1988) reported that the addition of chlorine dioxide to humic water can result in the production of MX at levels approximately 15% of those observed with chlorination. Use of chloramines resulted in the production of only 10 to 50% as much MX as produced by chlorination (Backlund et al., 1988). The same authors also reported that by increasing the proportion of chlorine dioxide in the combined chlorine/chlorine dioxide treatment, the concentrations of MX and EMX, and subsequent mutagenicity could be reduced.

2.3.2.3 Use of GAC to Remove Mutagenicity

GAC has been shown to be an effective means of removing mutagenic compounds produced following chlorination in a full-scale treatment process (Loper et al., 1985). Huck (1986) evaluated four disinfectants including chlorine and reported no mutagenicity breakthrough following GAC after a period of 6 months (10,450 bed volumes) in pilot studies conducted at Edmonton, Alberta. For the final two months GAC effluent was post-chlorinated; no mutagenic activity was reported from this step. In other pilot scale studies conducted by Huck et al. (1988) samples collected from GAC contactors at depths of 0.23 and 0.46 m which received chlorinated water were never shown to be mutagenic at the normal Ames test dose of approximately 5 liter equivalents with strain TA100. However incidents of revertant levels exceeding 1.5 times the background rate and mutagenic responses at higher doses were found to occur. Those responses obtained in samples collected from the 0.23 bed depth during a period in which the influent to the contactors contained high concentrations of organic material.

An investigation by Noordsij et al. (1985) evaluated GAC removal of mutagenicity in a situation where carbon was originally installed to remove taste and odour. Mutagenicity was completely removed for a period of more than two years following GAC treatment of a water shown to be mutagenic for TA98 (+S9) in both pH 2 and pH 7 XAD fractions. The identity of specific mutagens was however, not addressed.

Van der Gaag et al., (1982) reported no mutagenic activity in a chlorinated GAC effluent after 1,000 bed volumes for TA100 using pH 2 and pH 7 XAD extracts. Mutagenicity at pH 2 however was detected in the same filter after 3,000 bed volumes but was partially inactivated by S9. As in previously mentioned studies by others, no specific compounds were identified as major contributors to mutagenicity.

Monarca et al., (1983) examined mutagenicity removal by both virgin and partially exhausted GAC. In most cases specific mutagenic activities were lower in contactor effluents, indicating a selective removal of mutagenic compounds by the GAC. Mutagenicity removal was observed to be considerably better than TOC removal. Even after three months of operation when TOC removal decreased to 34%, mutagenicity activity removal exceeded 87%. The foregoing results suggest that mutagenicity removal on GAC may be site-specific: it will depend on the specific mutagens present, their concentrations, and the concentrations of other adsorbing/reacting substances.

A review of the literature clearly showed an identified need for further quantitation concerning the ability of GAC to remove specific compounds capable of causing mutagenicity. This research attempted to address this need by investigating the formation of the strongly mutagenic compound MX in conventional water treatment and its removal by GAC under conditions representative of typical operating procedure.

3.0 RESEARCH OBJECTIVES

This research examined activated carbon adsorption of the chlorination by-products trihalomethanes and MX under conditions representative of typical water treatment practice with specific attention to quantifying the effect of competition from background organics. The major objectives were to:

1) Obtain isotherm data for the adsorption of trihalomethanes and MX on GAC including competition from background organics

2) Evaluate Ideal Adsorbed Solution Theory to describe competitive adsorption effects for low THMs concentrations

3) Quantify the importance for trihalomethane adsorption of the slow fouling of GAC by natural organic matter (NOM)

4) Monitor breakthrough of trihalomethanes in full scale GAC contactors and compare observed removals to modelling predictions based on isotherm experiments

5) Investigate the occurrence and removal of MX in conventional water treatment practice

6) Quantify the removal of MX on activated carbon

7) Investigate the removal mechanism for MX on activated carbon.

4.0 MATERIALS AND METHODS

4.1 Chemical Preparation Methods

4.1.1 Solvents

For all analytical procedures, double distilled ethyl acetate, acetone, methanol, dichloromethane and hexane were used. Water was distilled, deionized with a Milli-Q® system and buffered to specified pH values using phosphate buffers (Fisher Scientific Alberta, Canada) unless otherwise stated. Displacer compounds benz[a]anthracene and benz[a]anthracene-7,12-dione (Sigma Chemical Company MO., USA) were used as received.

4.1.2 Standards

4.1.2.1 Trihalomethane Standard

Trihalomethanes mixture 601-M1, containing 0.2 mg/mL each of chloroform, bromodichloromethane, dibromochloromethane and bromoform in methanol was obtained from Supelco Canada (Oakville, Ontario). This was the stock standard used in all trihalomethane analyses, and the standard upon which the GC calibration was based.

4.1.2.2 MX and EMX Standards

Initially standards containing 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) at a concentration of 2.05 mg/mL and E-2-chloro-3(dichloromethyl)-4-oxo-butenoic acid (EMX) at a concentration of 0.18 mg/mL in ethyl acetate were provided by Dr. L.

Kronberg of the Åbo Akademi in Finland. Later, MX and EMX were synthesized at the University of Alberta Department of Chemistry according to a method described by Padmapriya (1985).

4.1.3 Adsorbates

Chloroform and bromoform were obtained in A.C.S. grade from Fisher Scientific Co., Fair Lawn, N.J. 07410. Bromodichloromethane and dibromochloromethane were obtained from the Aldrich Chemical Co. Inc., Milwaukee, Wisconsin 53233.

During the conduct of THM isotherm experiments solutions of either 2 µM/L or 20 µM/L were prepared in Milli-Q® water (Millipore Corp., Bedford, Mass.) or pre-GAC water obtained from the Buffalo Pound water treatment plant. Effluent from the Milli-Q® filtration system was further passed through a 1m x 2.5 cm dia. column of Filtrasorb 400® carbon prior to use.

Equivalent concentrations expressed in terms of µg/L are shown in Table 4.1.

The pH of the adsorbate solution was adjusted to 7.3±0.1 by the addition of 1.0 N NaOH and buffered using a 0.001 M potassium monobasic phosphate solution (Fisher Scientific, Fair Lawn, NJ 07410).

4.2 Activated Carbon Characterization Methods

4.2.1 Apparent Density Determination

Apparent density analyses were conducted on two of the carbons used in THM isotherm experiments. The purpose of

Table 4.1 Adsorbate Concentrations Used in Isotherm Experiments

Compound	Molecular Weight[a]	Initial Concentration (µg/L)	
		@ 2 µM/L	@ 20 µM/L
$CHCl_3$	119.37	239	2,387
$CHCl_2Br$	163.82	328	3,276
$CHClBr_2$	208.27	417	4,165
$CHBr_3$	252.72	505	5,054

[a] USEPA, 1984

conducting these analyses was to assess the effect of freeze drying on virgin carbon, and measure changes in apparent density attributable to pre-loading. Apparent density analyses were performed by G. Milne, Department of Civil Engineering, University of Alberta. Detailed methodology is presented in Appendix I.1. Results are discussed in Section 5.4.3.

4.2.2 Particle Size Distribution

Sieve analyses were conducted on each carbon as received and after washing to determine grain size distributions analyses by G. Milne, Department of Civil Engineering, University of Alberta. The methodology and results are presented in Appendix I.2.

4.3 Carbon Preparation Methods

4.3.1 Preparation of Carbon for Isotherm Experiments

The activated carbons selected for use in this study supplied by Calgon Carbon (Pittsburg, PA) were Filtrasorb 300® (F-300) and Filtrasorb 400® (F-400) and by Ceca Incorporated (Reno, NV) was Cecacarbon 830® (Ceca 830). The two Filtrasorb® carbons were also used in the pre-loading studies described later. Representative quantities of virgin GAC were obtained from the lot received using a riffle splitter. After splitting, the GAC was washed with Milli-Q® water to remove any fines and dried at 103°C for 16 hours. Powdered granular activated carbon (PGAC) was used in all isotherm experiments to reduce the time required to attain equilibrium (Randtke and Snoeyink, 1983). To produce PGAC,, the carbon was crushed using a Spex® mixer mill (Spex Industries, Inc., Edison, NJ. 08220) and sieved to obtain the fraction which passed a 325 mesh sieve but was retained on a 400 mesh sieve. The sieved fraction was then washed using organic free water to remove fines, centrifuged, and finally dried overnight at 103°C. The PGAC was then allowed to cool in a desiccator and stored in glass bottles with Teflon®-lined screw caps. PGAC was prepared by G. Milne, Department of Civil Engineering, University of Alberta. Specific details concerning the preparation method are shown in Appendix I.3.

Prior to use in THM isotherm experiments, pre-loaded carbon (F-300, Ceca 830) was freeze dried to reduce the moisture content. For MX isotherm experiments pre-loaded F-400 carbon was dewatered using centrifugation prior to use. For either type of isotherm experiment, the carbon was then crushed, sieved, and either a 325 x 400 mesh or 200 x 400 mesh fraction collected.

4.3.1.1 Drying Methodology

In order to properly sieve GAC and to obtain accurate weight measurements, it is necessary that the carbon be dry. Samples of partially exhausted Filtrasorb 300® and Ceca 830 from full-scale beds and the pre-loading column were received from Buffalo Pound. These samples were shipped in a wet state, and in order to dry them with minimal loss of adsorbed organics, freeze-drying rather than oven-drying was required. A Freezemobile 24 freeze-drier (VirTis Co., Inc. Gardiner, N.Y.) was used in cooperation with the microbiology department (University of Alberta) for this purpose. A complete description of the method used is detailed in Appendix I.4.

4.3.1.2 GAC Crushing Optimization

In order to determine the most efficient procedure for obtaining a representative sample of powdered granular activated carbon, an experiment was designed to examine the effects of 3 variables on the amount of carbon retained within a specified mesh size range. Using Filtrasorb 300® GAC, the crushing time, number of balls in the mill, and the size of the balls were varied until the goal of obtaining approximately 80% of the resulting PGAC within the 200-400 mesh size range was achieved. The optimal crushing parameters were determined to be 2 minutes using 64, 0.64 cm diameter balls. The exact procedure used and corresponding results are reported in Appendix I.5.

4.4 Pre-Loading Column Design and Operation

A column was designed for use in evaluating the reduction of GAC adsorptive capacity attributable to pre-loading of carbon with background organics. This "pre-loaded" carbon served to represent the carbon present in lower segments of the full-scale GAC beds where slow fouling with background organics occurs causing a reduction in capacity for specific organic compounds such as THM's. In past pilot scale studies conducted at Buffalo Pound (Andrews, 1987) rapid breakthrough of THMs was noted following exhaustion in the uppermost one-third of the bed.

In general, the design of the pre-loading column was patterned after one used in other studies (Crittenden, 1986). Only chemically inert materials including glass, teflon and stainless steel were used in construction. The assembly consisted of a glass outer column of approximately 5.0 cm internal diameter x 60.0 cm overall length which held ten individual stainless steel sample "boats" each containing carbon. The boats were held in place using custom made teflon end caps. Each boat was designed to contain 15 g (dry weight) of virgin F-300. The individual boats themselves were 5.0 cm diameter x 6.0 cm in length. The ends of each boat incorporated #100 mesh stainless steel screens. This allowed flow to pass unrestricted while retaining the carbon inside the boat.

Each boat was engraved with a consecutive number; indicating the order of removal 1A, 1B, 2A, 2B, 3A, 3B, 4A, 4B, 5A, or 5B. Boats designated A and B for each specific number were removed at the same time. Carbon from these boats was then combined to provide a suitable sample size. The volume of carbon contained in each boat represented approximately 75% of the empty boat volume. The excess 25% served to allow for bed expansion while operating in the upflow mode, thereby reducing the chance of screen plugging. This additional volume also allowed for a partial fluidization of the bed, should backwashing have been required. Complete pre-loading column preparation procedures are presented in Appendix I.6.1.

4.4.1 Pre-Loading Procedure for THM Experiments

Actual operation of the column at the Buffalo Pound water treatment plant commenced February 19, 1987 and continued for 16 weeks. Operational parameters are shown in Table 4.2.

The column was loaded, with boats 1A through 4B containing virgin Filtrasorb 300® carbon and with boats 5A and 5B containing Filtrasorb 300® carbon which was obtained from the top 0.3 m of a

Table 4.2 Pre-Loading Column Operating Parameters

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(1) Flow Direction - upflow

(2) Flowrate - 0.34 L/min (reset daily if required)

(3) Flowmeter - Gilmont model F1200, setting 51% of full scale

(4) Flowmeter Placement - immediately downstream of column

(5) Influent Source - GAC contactor influent (pre-chlorinated)

(6) Carbon Types:
- (i) Pre-washed Virgin F-300
- (ii) Pre-loaded F-300 from full-scale contactors (1986 operating season)

(7) Carbon Samples Used in Column:

Boats 1A, 1B - F-300 (Virgin)
2A, 2B - F-300 (Virgin)
3A, 3B - F-300 (Virgin)
4A, 4B - F-300 (Virgin)
5A, 5B - F-300 (Pre-loaded from 1986 summer and removed from full-scale contactor)

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full-scale contactor previously operated for 135 days. The schedule of removal designed as a geometric time series was:

Removal @ week 2 - boats 1A and 1B
Removal @ week 4 - boats 2A and 2B
Removal @ week 8 - boats 3A and 3B
Removal @ week 16 - boats 4A and 4B
- boats 5A and 5B

After each sample was removed, the carbon was placed in 40 mL glass vials and sealed with a screw top and teflon liner. The empty boat was then returned to the column such that the spacing and water tight seal would not be compromised.

Complete details regarding column influent and effluent are described in Appendix I.6.2.

4.4.2 Pre-Loading Column Procedure for MX Experiments

Influent water was obtained from a pilot plant designed to evaluate the mutagenic potential of alternative disinfectants (Huck et al., 1988). The water itself had been coagulated (with alum), flocculated, settled, and filtered through a dual media bed. The water was not exposed to any oxidants, in contrast to the water used in THM pre-loading work which had been pre-chlorinated. The column was operated at a velocity of 13.9 m/h (0.145 L/min), and in an upflow mode to prevent plugging and avoid the need for backwashing. The raw water source, the North Saskatchewan River, was of relatively good quality, with no upstream pulp and paper effluents (which could contain MX) or other significant industrial inputs.

In general, the column was operated in a similar manner to that described in Section 4.5.1 except virgin Filtrasorb 400® was placed in all sample boats.

4.5 Isotherm Methods

4.5.1 Isotherm Procedure

Adsorption isotherm experiments for both THM's and MX were conducted using the bottle point method. Appropriate amounts of PGAC (325 x 400 mesh for virgin carbon; 200 x 400 mesh for pre-loaded carbon) were weighed into either 1 L (THM's) or 0.160 L (MX) glass bottles prior to the addition of the adsorbate solution. Carbon dosages were approximately 2 to 100 mg/L. Spiked solutions were prepared in a 12.5 L stainless steel reservoir with a floating Teflon® cover (University of Alberta, Technical Services Department). All bottles were filled headspace free with the spiked water matrix and sealed with Teflon® lined caps. The bottles were placed in a rotary tumbler operated at 25 rpm to facilitate mixing. An equilibration period of six to seven days as described by Crittenden et al. (1985a) was used in all virgin carbon THM experiments. This time was also used in initial exploratory MX investigations (data not reported) but was later shortened due to the previously mentioned short half-life of MX in water. Because the MX decomposition rate decreases at lower pH values, MX isotherms were conducted at pH values representing the low end of the range in water treatment practice (6.5, and later 6.0).

Since temperature has been found to significantly affect loading capacity (Crittenden et al.,1985b), all experiments were conducted in a temperature controlled room at 20±1°C.

For THM isotherms, it was necessary to obtain a 40 mL supernatant aliquot from the 160 mL serum bottle immediately following equilibrium of isotherm bottles. This procedure was required to stop further contact of the liquid phase with the carbon and to provide a suitable sample size for storage at 4°C until GC analysis could be scheduled. Prior to removal of the 40 mL sample, centrifugation was employed to separate the carbon from the liquid phase. Due to the large number of sample bottles to be processed it was desirable to optimize the centrifugation parameters of time and rotational speed such that the most efficient separation could be obtained in a minimum amount of time.

The variables of centrifugation time and rotational speed were evaluated with the objective of minimizing carbon remaining in solution as measured by turbidity analyses in 40 mL samples. A centrifugation time of 30 minutes at 1800 rpm was finally selected for use in all isotherm experiments. Details of the evaluation procedure and results are presented in Appendix I.7.

For MX experiments, the PGAC was separated from the liquid phase immediately following equilibration by passing the solution through multiple glass wool plugs. The liquid phase was then analyzed for MX.

Initial adsorbate concentrations were determined using an average of isotherm blanks (i.e. bottles containing no carbon) typically included as every fourth bottle in the filling sequence of each isotherm experiment. Preparation and laboratory analyses for THM isotherm experiments were performed by G. Milne and D. Rector, Department of Civil Engineering, University of Alberta, and C. Rutledge, Women in Scholarship, Engineering and Technology student. Preparation and laboratory analyses for MX isotherm experiments were performed by D. Rector and C. Laverdure, Department of Civil Engineering, University of Alberta.

4.5.1.1 Equilibrium Time

For THM isotherms a kinetics experiment was designed to assist in the selection of an appropriate equilibration time. Individual isotherm bottles were filled with a solution containing 20 µM/L (2387 µg/L) of chloroform (a weakly adsorbing compound) and an appropriate amount of virgin carbon such that approximately 90% of the initial adsorbate would be removed. The bottles were equilibrated at 20°C, the temperature used in all isotherm experiments. After varying lengths of time (0-3 weeks) duplicate bottles containing the same carbon dosage were removed and the liquid phase analyzed. Removal was based upon blanks (bottles containing no carbon) equilibrated for a similar time period. Results showed that, within experimental error, equilibrium was reached in less than one day. However, to be consistent with equilibration periods reported by others (Crittenden et al., 1985a) an equilibration period of six to seven days was selected for use in all experiments involving virgin carbon. In isotherm experiments involving preloaded carbon the equilibration period was extended to two weeks.

A complete discussion concerning equilibrium kinetics for pre-loaded carbon is presented in Section 5.4.4.1.

A similar approach was initially applied to determine an appropriate equilibration time for MX isotherms. However due to the strong dependence of degradation rate on temperature and the low concentrations of MX used in isotherm experiments, a series of kinetics experiments was conducted prior to selection of equilibration periods. A detailed explanation of decomposition investigations is presented in Section 6.4.1.1.

4.5.1.2 Equilibrium Temperature

Since equilibration temperature has been found to significantly affect loading capacity (Crittenden et al., 1985b), all experiments were conducted in a temperature controlled room at 20 ± 1°C. This temperature represented an average value for Buffalo Pound water over the summer-fall GAC operating period.

4.5.2 Analysis of Isotherm Data

Following equilibration and analyses of liquid phase equilibrium concentrations, surface loadings (q_i) were calculated by taking a mass balance on the isotherm bottle:

$$q_i = (C_{io} - C_i)\ V/M \tag{4-1}$$

The variables C_{io} and C_i represent the initial and final liquid phase concentrations respectively for a particular adsorbate. Bottle volume was represented by V, and M designated the mass of PGAC present.

Data obtained from isotherm experiments were described using the Freundlich equation which relates solid phase concentrations to residual liquid phase concentrations as shown below for a specific adsorbate denoted as i:

$$q_i = K_i C_i^{1/n_i} \tag{4-2}$$

The Freundlich parameter K_i represents the adsorption capacity of the carbon for a specific adsorbate at a given equilibrium concentration C_i, whereas 1/n indicates the effect of concentration on adsorptive capacity. These parameters may be obtained by applying linear least squares (LLS) to a log transform of the data or as in the case of this study by applying non-linear least squares (NLLS) to untransformed data.

To optimize K and 1/n parameters, values of equilibrium concentrations which lay more than two standard deviations from the mean following linear regression using the MINITAB program (University of Alberta, Computing Services) were removed prior to calculation of initial K and 1/n estimates. The LLS estimates of K and 1/n based on data excluding outliers were then used as initial guesses to the UWHAUS program (University of Alberta, Department of Civil Engineering). The UWHAUS program generates NLLS square estimates of K and 1/n based on this input data.

It was observed that the outlying values had little influence on the LLS estimation procedure which is based on log-transformed input values, but greatly influenced NLLS estimates based on untransformed data. In general only one to three outlying input values were observed in each set of approximately thirty data which comprised each extended single solute data set. Typically these outlying values displayed equilibrium concentration values, C_e, which were lower than expected and correspondingly yielded higher than expected calculated equilibrium concentration values, Q_e. The suspected source of this problem was loss of volatiles from poorly sealed isotherm bottles or storage vials containing the extracted samples. To better assist in observing these suspect values a plotting routine was incorporated into the LLS (MINITAB) program. This subcommand causes the standardized residuals to be plotted each time the program is run thus alerting the user to any suspect input values. In addition, the UWHAUS program was modified to output a file containing residual sum of squares values and fitted values. These could then be plotted allowing the user to observe data variance.

4.6 Chemical Analytical Methods

4.6.1 Total Organic Carbon

Samples for total organic carbon (TOC) analysis were acidified to pH 2 immediately following collection and stored at 4°C in 500 mL glass bottles sealed with Teflon® lined caps until analyzed. Acid was added to inhibit bacterial growth which could cause a reduction in the concentration of organic carbon (OC) and an increase in inorganic carbon (IC). As many of the samples were high in IC as opposed to OC, acidification resulted in conversion of IC such that:

$$CO_3^{=} \rightarrow HCO_3^{-} \rightarrow H_2CO_3 \leftrightarrow CO_2\uparrow + H_2O$$

Since replicate analyses were conducted, samples were exposed to atmosphere between analyses. Samples analyzed later in time could exhibit lower IC values due to volatilization of CO_2. Therefore prior to all analyses, the samples were purged for approximately 8 to 10 minutes with prepurified nitrogen to remove as much of the CO_2 as possible. Analyses were performed with a Dohrmann DC-80® TOC Analyzer (Xertex Corp., Santa Clara, CA) utilizing UV-promoted persulfate oxidation followed by IR detection of the resulting carbon dioxide as recommended in Standard Methods (APHA, 1985). The samples were analyzed for total carbon (TC) and inorganic carbon (IC) and these values were subtracted to arrive at the TOC. The purging procedure however, also reduces volatile OC from the samples. Therefore, the TOC reported specifically refers to the non-volatile organic carbon (NVOC) fraction. Because of the type of organic matter being analyzed, there was no reason to assume that the volatile fraction would constitute a large fraction of the OC.

The following quality control program was used: fresh standard solutions were prepared weekly. Before preparation, the standards KHP (for total carbon), sodium carbonate (for inorganic carbon) and potassium persulfate were heated at 103°C overnight. The DC 80 analyzer was calibrated daily in both TC and IC modes with 6 to 8 injections each, and checked again between sample analyses. An average of 3 replicates was obtained for each sample.

TOC analyses were performed by G. Milne, D. Rector and C. Laverdure, Department of Civil Engineering, University of Alberta.

4.6.2 Total Organic Halides

Total organic halides (TOX) were measured using the adsorption-pyrolysis-titrimetric method as described in Section 506 of Standard Methods (APHA, 1985). TOX analyses were performed by G. Milne, D. Rector and C. Laverdure, Department of Civil Engineering, University of Alberta. A Xertex-Dohrmann DX-20® Total Organic Halide Analyzer was utilized for this application. Samples were preserved by addition of sodium thiosulfate upon collection to neutralize any remaining disinfectant residual and stored at 4°C until analysis.

4.6.3 Chlorine

Both free and combined chlorine (monochloramine and dichloramine) residuals were determined as per Method 408C (Chlorine Residual/Amperometric Titration) in Standard Methods (APHA, 1985) with a Wallace and Tiernan (Pennwalt Corporation, Scarborough, Ontario) Series A-790 Amperometric Titrator using 0.0250 N sodium thiosulfate as the titrant. Chlorine analyses were performed by S. Daignault, Department of Civil Engineering, University of Alberta.

4.6.4 Trihalomethanes

The four THM components were analyzed according to EPA method 501.1. A Hewlett Packard Model 5790A gas chromatograph equipped with a flame ionization detector (FID) was used in conjunction with a Teckmar liquid sample concentrator (LSC-2) and autosampler (ALS) and a Hewlett Packard Model 3390A integrator. This setup was used for all analyses during the period of January 1986 to May 1987. In May 1987, a new GC and integrator were received. A Varian 3300 GC and Spectra-Physics SP4290 integrator replaced the older Hewlett Packard GC and integrator. All subsequent analyses were performed on the new equipment. Details concerning specific operating parameters, instrument calibration, and quality control procedures are presented in Appendix II.

4.6.5 MX and EMX

Analytical procedures for MX and EMX were adapted from those outlined by Kronberg et al. (1988) and Horth et al. (1987b). In general, each 1 L sample solution was acidified to pH < 2 with 2 M sulfuric acid and extracted with 3 aliquots of ethyl acetate (250 mL, 150 mL, 150 mL) in 2 L glass separatory funnels with Teflon® fittings. Solvent volumes for samples other than 1 L were proportional to these. Water was removed from the extracts by passage through filters of sodium sulfate crystal. The extract volumes were reduced to approximately 1 mL by rotary evaporation followed by further evaporation to dryness under a gentle stream of nitrogen. Initially, 653 ng mucobromic acid (MBA) in ethyl acetate was added to these extracts as an internal standard. This amount was later approximately doubled when it became apparent that larger amounts of internal standard produced more consistent results.

The concentrated extracts were methylated with 0.5 to 1 mL 2% sulfuric acid (v/v) in methanol. The vials were sealed with Teflon® lined caps and heated to 70°C for 60 minutes. The solutions were cooled and then quenched with 1 to 2 mL of 2% (m/v) sodium bicarbonate in water until neutral pH was attained. The derivatized product was extracted with three 1 mL portions of hexane, dried with sodium sulfate crystal and reduced to approximately 100 µL final volume by evaporation under a gentle stream of nitrogen.

All final extracts were analyzed by gas chromatography (GC) using the following conditions. A Hewlett Packard 5790A gas chromatograph with a ^{63}Ni electron capture detector (ECD) was equipped with a fused silica DB-1 capillary column (30 m x 0.25 mm I.D., 0.25 µm methyl silicone film thickness; J&W Scientific, Folsom, CA., USA) for analysis. The carrier/make-up gas used was 5% methane in argon with a carrier head pressure of 12 psi (flowrate approximately 1 mL/min). Mode of injection was split using a 5:1 ratio. GC conditions were as follows: injector and detector temperatures were 220°C and 300°C respectively, oven temperature program was 150°C, 8.5 min hold, 10°C/min to 275°C, 5 min hold. Injection volume was typically 3 µL and a 1 µL hexane solvent wash was employed.

Selected samples were analyzed by GC/MS using a VG Analytical 7070E mass spectrometer operated in electron ionization mode at 70 eV ionization energy. Chromatographic separation was achieved with a 60 m DB-1 capillary column (0.25 mm ID, 25 µm methyl silicone film thickness) operated initially at 100°C for 2 min and then temperature programmed to 250°C at 10°C/min. The carrier gas used was helium with a head pressure of 10 psi (flowrate approximately 1 mL/min). The outlet of the GC column was inserted directly into the mass spectrometer ionization chamber, held at a temperature of 250°C. GC/MS analyses were performed by S. Daignault, Department of Civil Engineering, University of Alberta. Agreement to within 15% of the fragment ion intensity ratios established by Kronberg et al. (1988) was taken as confirmed identification of MX and EMX.

4.7 Water Treatment Plant Sampling for MX

A total of six water treatment plants were selected for MX sampling (Figure 4.1). Excluding Plant B all plants were chosen because of high influent TOC concentrations and/or the use of a pre-chlorination step. Plants A, C and F practiced both pre-chlorination and post-chlorination (Plant C following GAC treatment). Plant D employed post-chlorination only while Plant E employed post-chloramination. Plant B used both chlorine dioxide and chloramines for disinfection, however this plant was only sampled at the raw water position (prior to the addition of any disinfectant).

For five of the six plants, samples were collected from both raw and finished water. The date and location at which samples were collected in individual treatment plants is shown in Figure 4.1. For preservation, concentrated sulfuric acid was added immediately following collection to all samples until a pH of 2 was reached and storage was at 4°C prior to analysis. Samples obtained from treatment plants that did not practice pre-chlorination were chlorinated in the laboratory to assess the potential for production

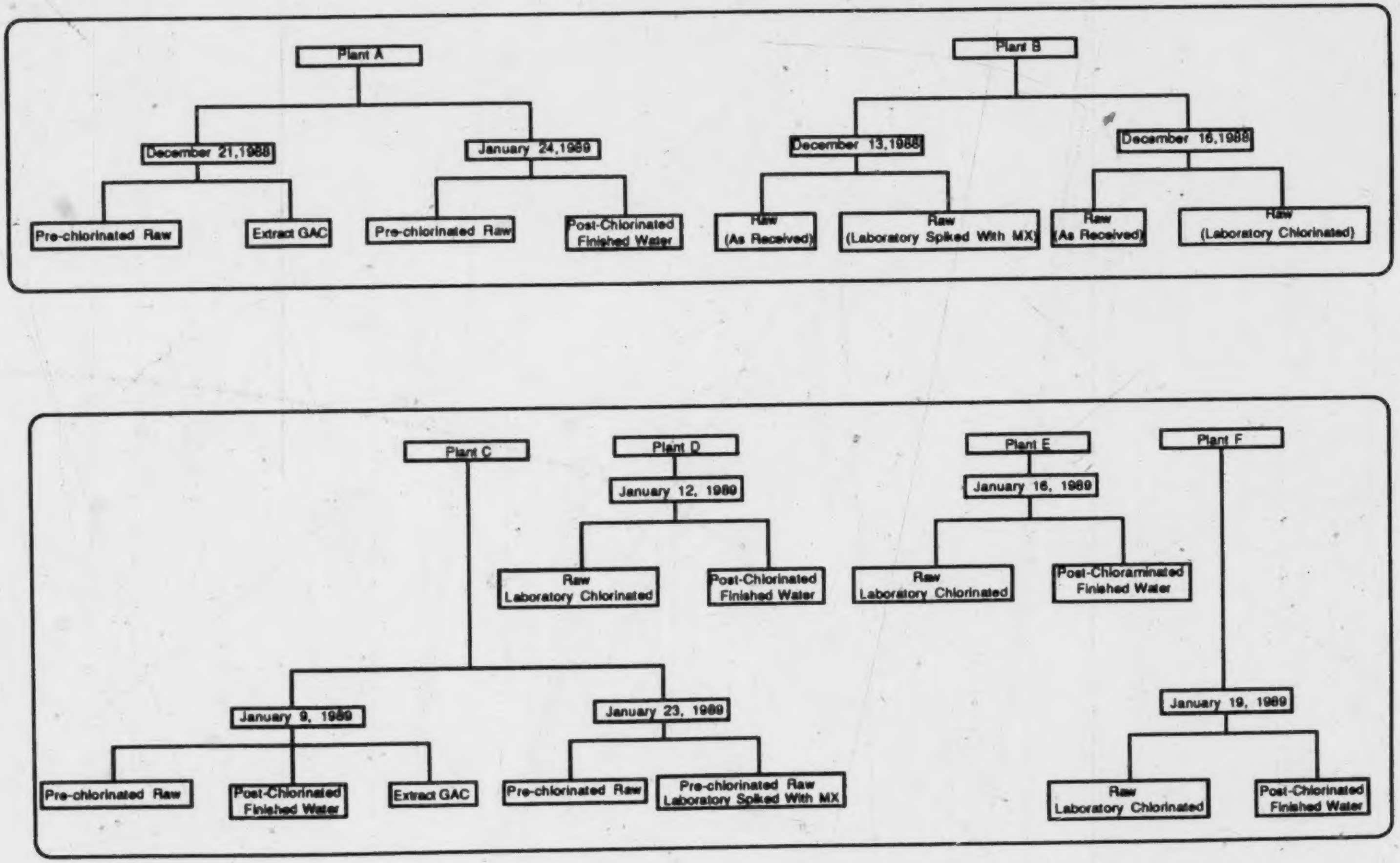

Plant A
December 21,1988
Pre-chlorinated Raw
Extract GAC
January 24,1989
Pre-chlorinated Raw
Post-Chlorinated Finished Water
Plant B
December 13,1988
Raw (As Received)
Raw (Laboratory Spiked With MX)
December 16,1988
Raw (As Received)
Raw (Laboratory Chlorinated)
Plant C
January 9, 1989
Pre-chlorinated Raw
Post-Chlorinated Finished Water
Extract GAC
January 23, 1989
Pre-chlorinated Raw
Pre-chlorinated Raw Laboratory Spiked With MX
Plant D
January 12, 1989
Raw Laboratory Chlorinated
Post-Chlorinated Finished Water
Plant E
January 16, 1989
Raw Laboratory Chlorinated
Post-Chloraminated Finished Water
Plant F
January 19, 1989
Raw Laboratory Chlorinated
Post-Chlorinated Finished Water

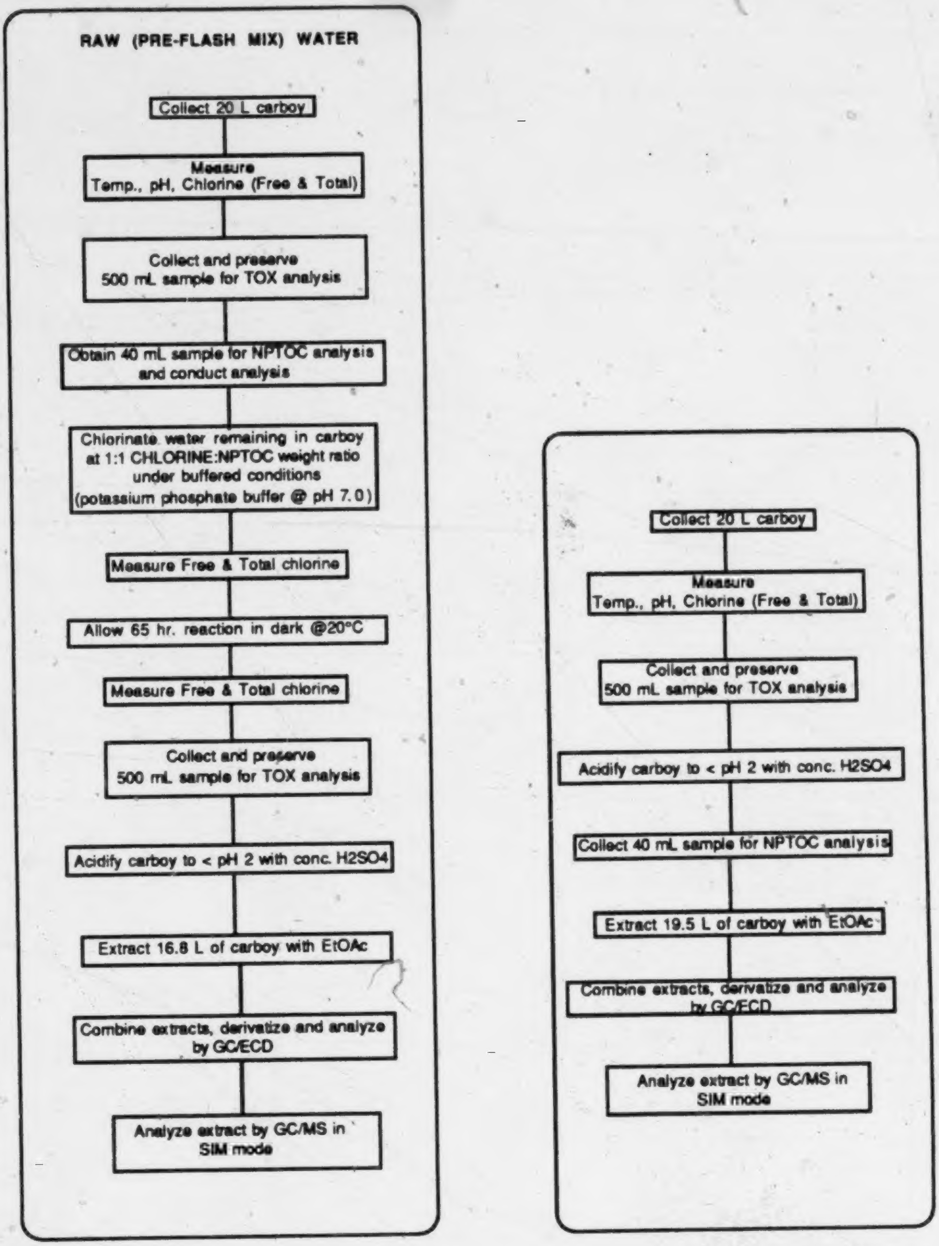
Figure 4.1 Water Treatment Plant Sampling Protocol

of MX and EMX and also to provide a direct comparison to other plants which routinely employed pre-chlorination as part of their treatment process. Laboratory chlorination was carried out at a 1:1 chlorine to TOC weight ratio and pH was adjusted to 7.0 using a potassium phosphate buffer solution (Kronberg et al., 1985; Hemming et al., 1986). Samples were allowed to react for 40 to 60 hr at 20°C before being acidified to pH 2 and extracted with ethyl acetate. Sample handling and analysis protocols are shown in Figures 4.2(a) and 4.2(b). Large volume extractions and MX analyses were performed by C. Laverdure and S. Daignault, Department of Civil Engineering, University of Alberta.

4.8 Soxhlet Extraction of GAC for MX and EMX

In water treatment plants A and C, both of which use GAC, the raw water was chlorinated, giving a potential for MX formation and subsequent removal on the GAC. Soxhlet extractions were conducted by C. Laverdure, Department of Civil Engineering, University of Alberta, using GAC obtained from both plants, to determine if any MX could be recovered. The Soxhlet method in general followed a procedure used by Gammie (1987) to extract organic compounds including geosmin from GAC. A similar extraction method was used by Loper et al. (1985) to recover mutagenic compounds from GAC.

A sample of GAC from Plant A was obtained on December 14, 1988, from approximately mid-depth in the contactor. The GAC in that contactor was a mixture of approximately 80-90% Filtrasorb 300® carbon and 10-20% Ceca 830 carbon. Excess moisture was removed by centrifugation of the GAC upon receipt at the laboratory,


RAW (PRE-FLASH MIX) WATER
Collect 20 L carboy
Measure Temp., pH, Chlorine (Free & Total)
Collect and preserve 500 mL sample for TOX analysis
Obtain 40 mL sample for NPTOC analysis and conduct analysis
Chlorinate water remaining in carboy at 1:1 CHLORINE:NPTOC weight ratio under buffered conditions (potassium phosphate buffer @ pH 7.0)
Measure Free & Total chlorine
Allow 65 hr. reaction in dark @20°C
Measure Free & Total chlorine
Collect and preserve 500 mL sample for TOX analysis
Acidify carboy to < pH 2 with conc. H2SO4
Extract 16.8 L of carboy with EtOAc
Combine extracts, derivatize and analyze by GC/ECD
Analyze extract by GC/MS in SIM mode
Collect 20 L carboy
Measure Temp., pH, Chlorine (Free & Total)
Collect and preserve 500 mL sample for TOX analysis
Acidify carboy to < pH 2 with conc. H2SO4
Collect 40 mL sample for NPTOC analysis
Extract 19.5 L of carboy with EtOAc
Combine extracts, derivatize and analyze by GC/ECD
Analyze extract by GC/MS in SIM mode

(a) (b)

Figure 4.2 Sample Handling and Analysis Protocol: (a) Raw Water and (b) Pre-Chlorinated and Post Chlorinated Water

and the sample was stored at 4°C prior to the determination of moisture content and subsequent Soxhlet extraction. Results of all carbon extractions are expressed on the basis of dry carbon weight by correcting for the moisture content present at the time of analysis.

A sample of GAC (Norit 820®) was collected from the top 0.2 m of one of the filter-adsorbers of Plant C at the same time that samples of raw and finished water were obtained. The sample was drained of excess water and stored in an amber glass bottle with a Teflon® lined cap at 4°C in the dark. To reduce the possibility of MX degradation during storage for both of the GAC samples, moisture content analyses were conducted the same day as sample collection, permitting Soxhlet extractions to begin in less than 24 hours.

The general Soxhlet analysis method consisted of weighing out 50 g of GAC and placing it into a Soxhlet extraction unit. The extraction unit consisted of a 40 mm I.D. Soxhlet extraction tube connected to an Allihn type condenser and a 1 L round bottom flask. Prior to use the entire apparatus was washed with triple distilled dichloromethane by allowing the solvent to cycle for a period of approximately 24 hours. To avoid losses of MX due to possible adsorption, an extraction thimble was not used, instead a small amount of glass wool was placed in the bottom of the Soxhlet unit. The glass wool had been previously Soxhletted for a period of 24 hours with ethyl acetate and allowed to air dry. After adding the carbon to the Soxhlet unit a further glass wool plug was placed at the top of the siphon to avoid carbon losses. After adding 350 mL of triple distilled dichloromethane to the round bottom flask, the complete unit was assembled and allowed to cycle at approximately 4 cycles per hour by adjusting the rheostat controlling the heater. Soxhletting was continued for approximately 24 hours. The solvent was then concentrated using rotary evaporation. The resulting extract was taken to dryness under a gentle stream of nitrogen in a 1 dram vial, derivatized as previously described and filtered using a 1 mL syringe equipped with a 0.45 µm Teflon® filter adaptor (Gelman Sciences: Acro LC35). Analyses were conducted using both GC/ECD and GC/MS.

5.0 PREDICTION OF TRIHALOMETHANE ADSORPTION ON GAC IN THE PRESENCE OF BACKGROUND ORGANICS AT A LARGE DRINKING WATER TREATMENT PLANT

The process of using activated carbon to remove trihalomethanes, formed as a result of chlorinating water containing organic precursors, was evaluated in terms of predicting their removal at the Buffalo Pound water treatment plant, located near Moose Jaw, Saskatchewan. The ability of ideal adsorbed solution theory to predict competitive interactions for low concentrations of trihalomethanes in both organic-free and actual surface waters was investigated using computer models. Of primary interest was the estimation of the adsorptive capacity reduction in the lower two thirds of GAC beds which was attributed to slow fouling by background organics. This was addressed by the construction of a specially designed "pre-loading" column which allowed a sample of GAC to come in contact with the same water received by the full-scale beds. Samples of carbon pre-loaded with background organics were then examined using isotherm experiments to measure the residual capacity for trihalomethanes. Experimentally determined adsorption characteristics were used in conjunction with various computer models to simulate the performance of full-scale beds. Comparison of computer generated prediction-to-breakthrough concentration data collected at various bed depths illustrated the usefulness of this approach in explaining the apparent reduction of bed capacity following normal operation.

5.1 Process Configuration and Routine Operation

A brief description of the Buffalo Pound water treatment plant, including the GAC contactors, is presented in this section. A more comprehensive discussion including operation of the carbon regeneration facilities is presented elsewhere by Gammie and Giesbrecht (1987).

The conventionally designed treatment facility includes pre-chlorination, alum coagulation/flocculation with polymer aids, settling in upflow reactor type clarifiers equipped with 60° tube settlers, pH correction, and mixed media filtration (Figure 5.1). The plant, located at the raw water source, supplies the Cities of Regina and Moose Jaw, Saskatchewan with 54 and 136 m^3/day through 50 km and 20 km of pipeline respectively.

In 1984/1985 GAC contactors were added to the treatment process immediately following the multimedia filters. The eight individual contactors each contain 172 m^3 of GAC, have a surface area of 58.5 m^2 and a depth of 3.05 m. Each contactor is equipped with plastic underdrains covered with a 0.5 mm wire mesh. The contactors were designed to operate at a minimum empty bed contact time (EBCT) of 15 min. Operating parameters are presented in Table 5.1. Contactor effluent is collected in a clearwell located underneath the contactors where it is post-chlorinated using a flow-paced chlorinator prior to distribution.

Normally, the contactors are operated only part of the year (typically June to November) when taste and odour problems most frequently occur. They are backwashed approximately once per month to prevent excessive headloss build-up and to reduce

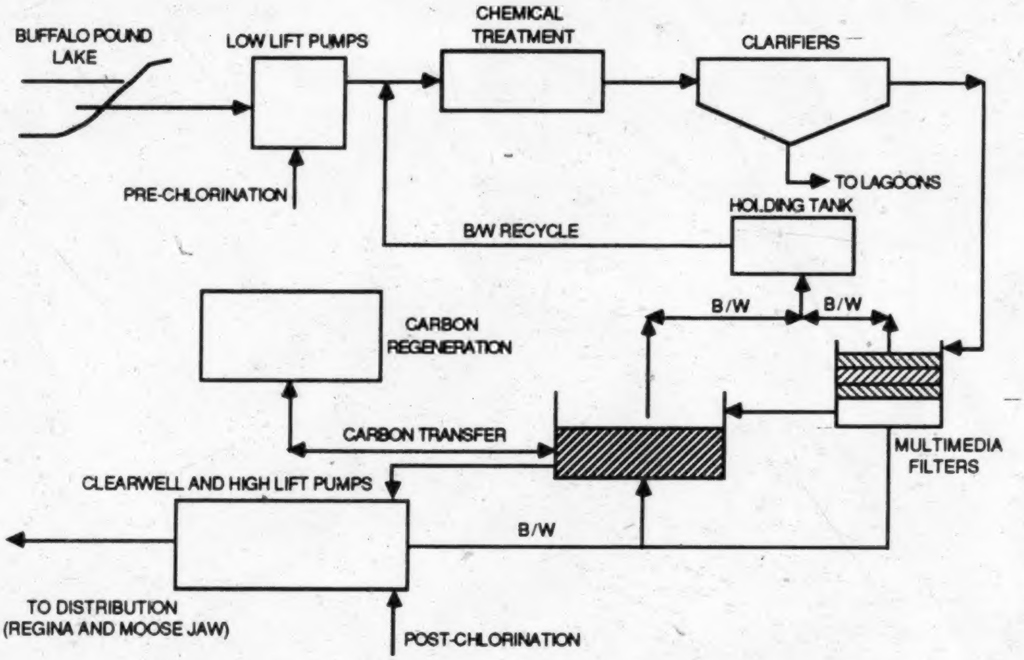

BUFFALO POUND LAKE
LOW LIFT PUMPS
CHEMICAL TREATMENT
CLARIFIERS
PRE-CHLORINATION
TO LAGOONS
HOLDING TANK
B/W RECYCLE
B/W
B/W
CARBON REGENERATION
CARBON TRANSFER
MULTIMEDIA FILTERS
CLEARWELL AND HIGH LIFT PUMPS
B/W
TO DISTRIBUTION (REGINA AND MOOSE JAW)
POST-CHLORINATION

Figure 5.1 Buffalo Pound Plant Schematic
(Adapted from Gammie and Giesbrecht, 1987)

Table 5.1 GAC Contactor Operating Parameters

Parameter	Value
Number of Beds	8
Volume of GAC/Bed	172 m^3
Weight of GAC/Bed	86,000 kg
Total Carbon Weight	689,000 kg
Bed Depth	3.05 m
Bed Surface Area	58.5 m^2
Design Flow	12.2 m/hr
Flow Range (Actual)	4.4 - 11.7 m/hr
EBCT @ 5.9 m/h (2 gpm/ft^2)	31.1 min
EBCT @ 11.7 m/h (4 gpm/ft^2)	15.6 min

After Gammie and Giesbrecht (1987)

the number of bacteria present in the effluent as defined by standard plate counts. On the basis of headloss alone, the contactors could, if desired, be operated for periods of up to 14 weeks before headlosses of 3.7 m to 4.6 m would necessitate backwashing. During backwash, water is drawn from the clearwell and pumped into the contactors at a design flow of 54 m/h.

5.2 Monitoring of Specific Parameters

The GAC contactors at Buffalo Pound are monitored on a continuous basis for operational problems, flow, turbidity and headloss, and daily for pH, chlorine residuals and standard plate counts. In addition, monitoring is conducted at least weekly for TOC, TTHM's (including individual components), odour, particle counts, geosmin, algae cells, and phosphate at the effluent from each of the contactors and at selected ports from one of the contactors.

5.3 Single Solute Isotherms and Freundlich Parameter Estimation

Single solute adsorption isotherms were conducted using initial concentrations of both 2 and 20 µM/L for chloroform, bromodichloromethane, dibromochloromethane and bromoform on the three commercially available carbons. Two of these carbons; the Filtrasorb 300® (F-300) and Ceca 830 are used in the full scale GAC treatment process at Buffalo Pound. The third carbon, Filtrasorb 400® (F-400) has been studied by others for removal of similar organic compounds (Cairo et al., 1979) and as such acted as a alternative carbon to provide comparative data for this study.

Experimental conditions and laboratory data for individual isotherms are presented by Huck and Andrews (1988). Typical isotherms and summary plots for the three carbons are shown in Figures 5.2 to 5.7.

In order to obtain a wide range of single solute isotherm data, separate experiments were conducted using initial concentrations of 2 µM/L and 20 µM/L each for the four individual trihalomethane components. The data were then combined to form a single extended isotherm plot for each component. In most cases an attempt was made to overlap the data of the individual experiments. An example of two data points from separate experiments coinciding is shown in Figure 5.2 at a liquid phase concentration of approximately 85 µg/L. The combining of data for extended isotherms was necessary to provide a wide range of single solute data for subsequent predictions using IAST in addition to allowing better estimates of Freundlich parameters. A discussion of the statistical approach used to determine the Freundlich parameters K and 1/n was presented in Section 4.5.2.

Single solute isotherm parameters for experiments conducted in organic free water and their associated 95% confidence intervals are listed in Table 5.2.

Freundlich parameters obtained for the adsorption of individual THM's on the three carbons are discussed in the sections which follow.

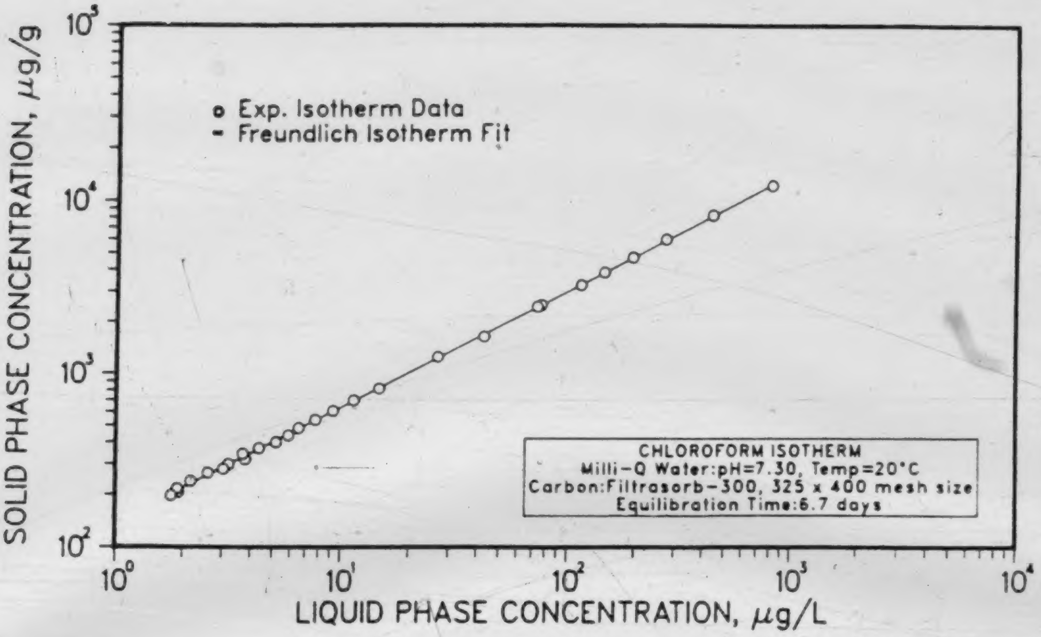


Figure 5.2 Typical Extended Single Solute Isotherm for Chloroform

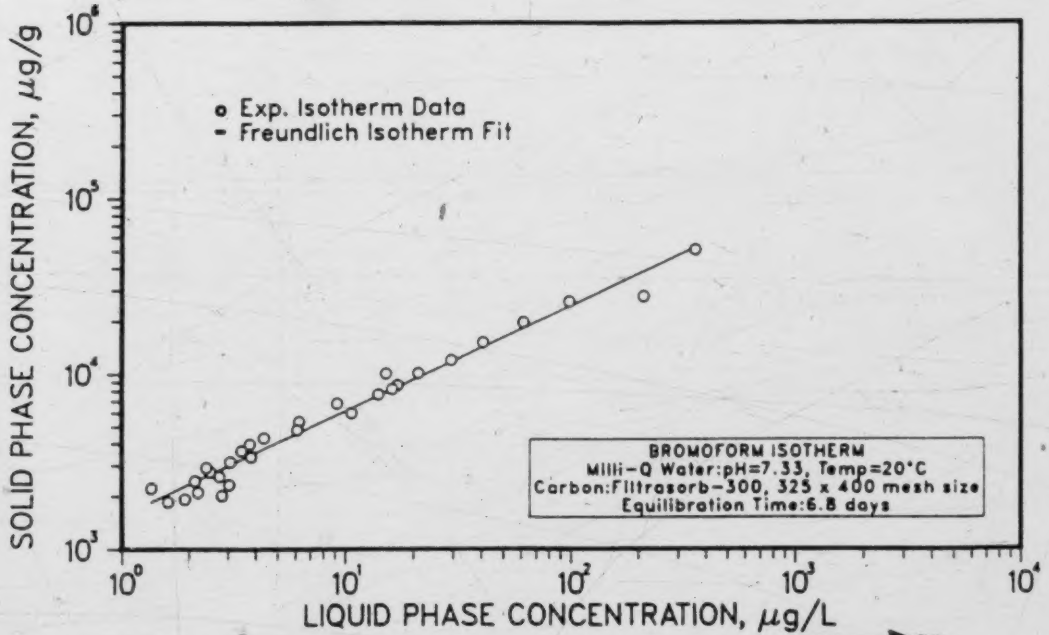


Figure 5.3 Typical Extended Single Solute Isotherm for Bromoform

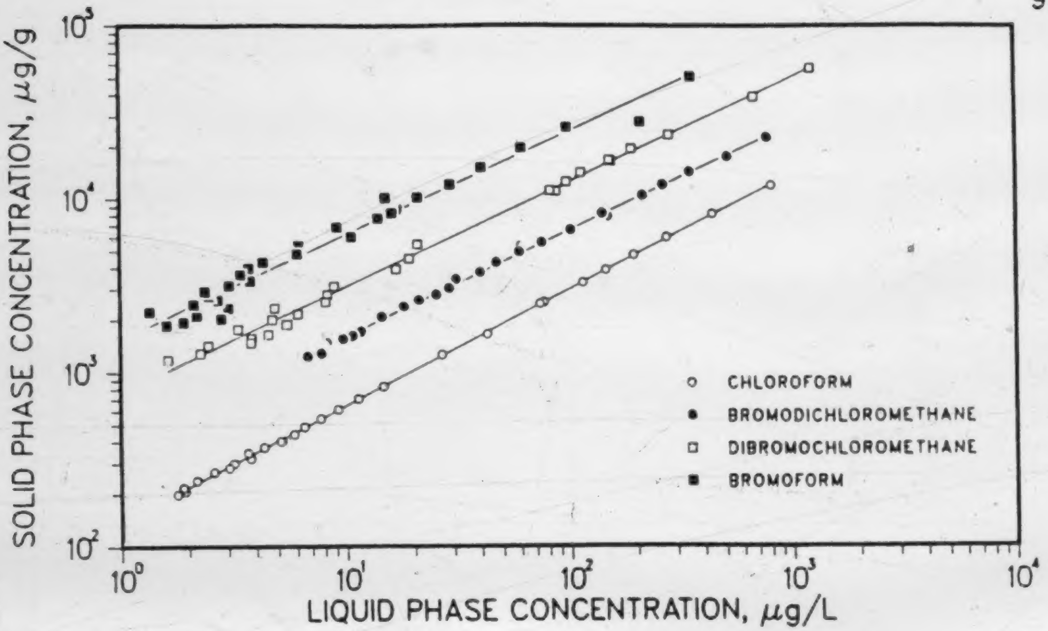


Figure 5.4 Comparison of Trihalomethane Isotherms Using F-300 Carbon

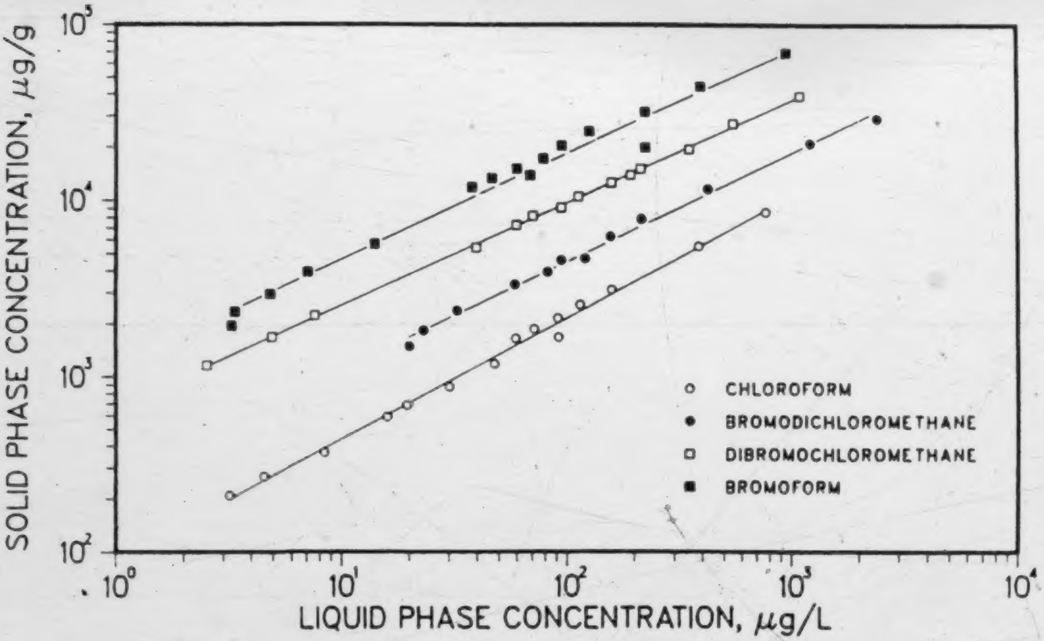


Figure 5.5 Comparison of Trihalomethane Isotherms Using Ceca 830 Carbon

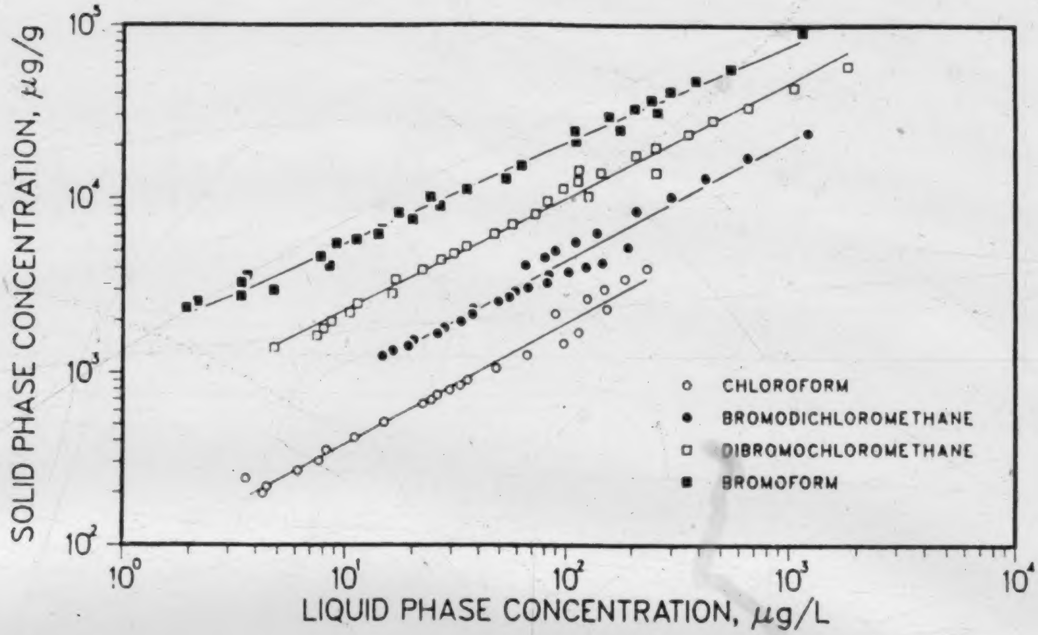


Figure 5.6 Comparison of Trihalomethane Isotherms Using F-400 Carbon

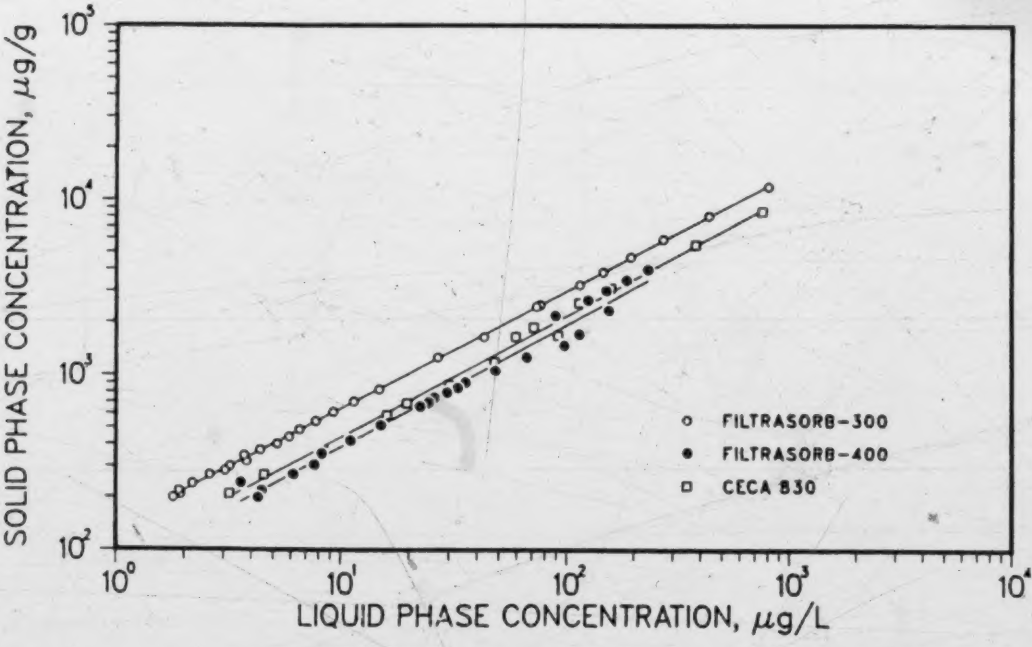


Figure 5.7 Comparison of Chloroform Isotherms Using F-300, Ceca 830and F-400 Carbons

Table 5.2 Single Solute Isotherm Parameters and 95% Confidence Intervals

a. Isotherm Results For Filtrasorb 300®

Compound	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range ($\mu g/L$)
Chloroform	6.7	7.30	143	139-147	0.662	0.658-0.668	1.8-807
Bromodichloromethane	6.6	7.30	401	383-419	0.607	0.599-0.614	6.7-773
Dibromochloromethane	6.9	7.30	801	760-842	0.599	0.591-0.607	1.6-1230
Bromoform	6.8	7.33	1790	1430-2160	0.558	0.519-0.598	1.6-354[a]

b. Isotherm Results For Ceca 830

Compound	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range ($\mu g/L$)
Chloroform	6.7	7.30	79.5	41.5-118	0.705	0.627-0.782	4.6-759
Bromodichloromethane	6.6	7.30	355	288-421	0.568	0.543-0.594	20.0-2390
Dibromochloromethane	6.9	7.30	643	589-697	0.589	0.576-0.602	2.5-1070
Bromoform	6.8	7.30	1590	1220-1970	0.544	0.512-0.575	3.3-3090

c. Isotherm Results For Filtrasorb 400®

Compound	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range ($\mu g/L$)
Chloroform	6.4	7.32	57.3	43.8-70.9	0.769	0.728-0.809	4.3-612
Bromodichloromethane	6.8	7.30	193	149-237	0.683	0.647-0.719	14.7-1200
Dibromochloromethane	6.9	7.29	699	581-818	0.592	0.567-0.617	4.8-1820
Bromoform	6.6	7.37	1623	1370-1877	0.559	0.536-0.582	1.9-2060

Carbon size: 325 x 400 mesh Temperature: 20°C

[a] The narrow range obtained for this component was a result of a lack of sample results at high liquid phase concentrations.

* NLLS: Non Linear Least Squares

5.3.1 Filtrasorb 300®

A review of the Freundlich parameter data presented in Table 5.2 and Figure 5.4 shows that the K parameter (adsorptive capacity) at unit concentration varies dramatically with respect to individual trihalomethane components. For instance, bromoform, the strongest adsorbing compound, exhibits a K value of approximately 2.2, 4.5 and 12.6 times that reported for dibromochloromethane, bromodichloromethane and chloroform respectively. The adsorptive capacities of the carbon for the four compounds are statistically different. This is apparent since the 95% confidence intervals (CI's) do not overlap. CI's for 1/n parameter values overlap slightly for the three most strongly adsorbing compounds. However, due to the narrow confidence bands for K values the adsorptive capacities may be viewed as being significantly different.

5.3.2 Ceca 830

Similar adsorptive capacity trends for the four trihalomethane components were noted for the Ceca 830 carbon (Table 5.2 and Figure 5.5). In this case bromoform, the strongest adsorbing compound, displayed an adsorptive capacity (Table 5.2) that was 2.5, 4.5, and 20.0 times the capacity of dibromochloromethane, bromodichloromethane and chloroform respectively when adsorbed individually. Confidence intervals for the adsorptive capacity parameter K are well defined and do not overlap. As for F-300, the 1/n confidence bands are narrow but do overlap to some degree. Because the adsorptive capacities are well-defined, the THMs may be considered to adsorb significantly differently from each other.

5.3.3 Filtrasorb 400®

Relative adsorptive capacities of the four THM's followed the same trend as the two carbons discussed previously (Table 5.2 and Figure 5.6). Well defined, non-overlapping confidence bands for K show that the equilibrium capacities are significantly different. Confidence bands for the slope parameter, 1/n, overlap slightly for only bromoform and dibromochloromethane. For this carbon relative adsorbabilities show that bromoform, the strongest adsorbing compound, will be adsorbed 2.3, 8.4, and 28.3 times more strongly than dibromochloromethane, bromodichloromethane and chloroform respectively.

5.3.4 Comparisons of Freundlich Parameter Estimates Among Carbons

Direct comparisons of Freundlich parameters among isotherms should not be made without some caution. The structure of the Freundlich model ensures a high correlation between estimates of K and 1/n (i.e. one parameter can be varied to compensate for a change in the other and yield almost the same predicted values). For this reason K values should not be compared without also comparing the corresponding 1/n values. By convention, K values are evaluated at a liquid phase equilibrium concentration of 1. In cases where exprtimental data did not extend to this low concentration, K values were obtained using extrapolations. It should also be noted that K and 1/n values obtained for isotherms containing mixtures of adsorbates are valid only for the specific initial concentration of each component used in the experiment.

The relative adsorptive capacity of individual carbons for specific THM components may be determined from a review of Table 5.2, Figures 5.8 and 5.9 and Appendix III. Equilibrium capacities for chloroform, bromodichloromethane, dibromochloromethane and bromoform were highest for the F-300 carbon. For chloroform, these capacities were respectively 1.8, 1.1, 1.2, 1.1 times higher than for adsorption of the same compounds on Ceca 830 and 2.5, 2.1, 1.1, 1.1 times higher respectively than the capacity of F-400. Similar comparisons for the three other compounds are shown in Appendix III. Adsorption capacities of both chloroform and bromodichloromethane may be judged as being significantly different for the three carbons since the confidence bands for neither K nor 1/n overlap. Capacities for dibromochloromethane and bromoform were not significantly different since the confidence bands for K and in most cases 1/n are noted to overlap.

In all cases it must be noted that the equilibrium capacity results are valid only for the experimental conditions actually tested. A change in pH or temperature would definitely affect the adsorptive capacities.

5.4 Prediction of Multicomponent Equilibrium of Known Trihalomethane Mixtures

The use of Ideal Adsorbed Solution Theory (IAST) was examined in predicting multicomponent interactions of trihalomethane adsorption on activated carbon.

IAST allows competitive adsorption results to be predicted for multicomponent mixtures of known concentration using single solute

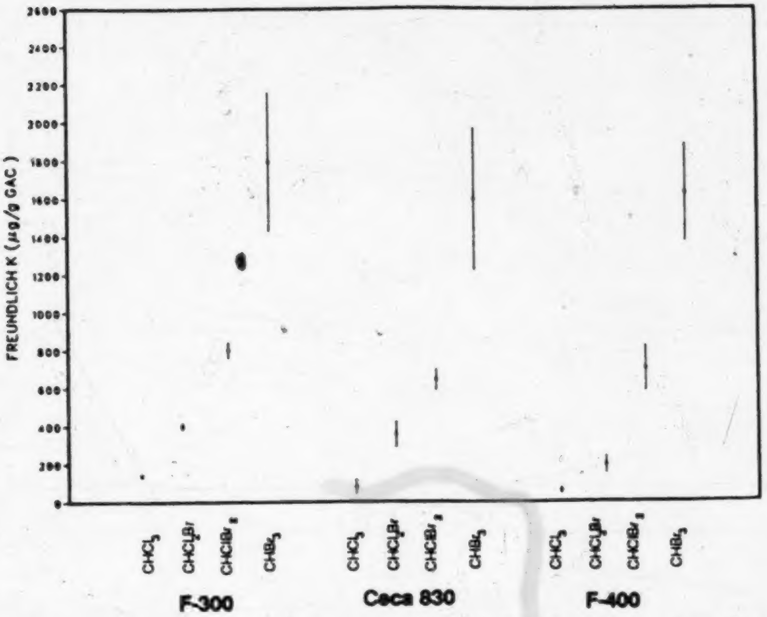


Figure 5.8 Summary of Freundlich K Parameters for Carbons Used in the Study

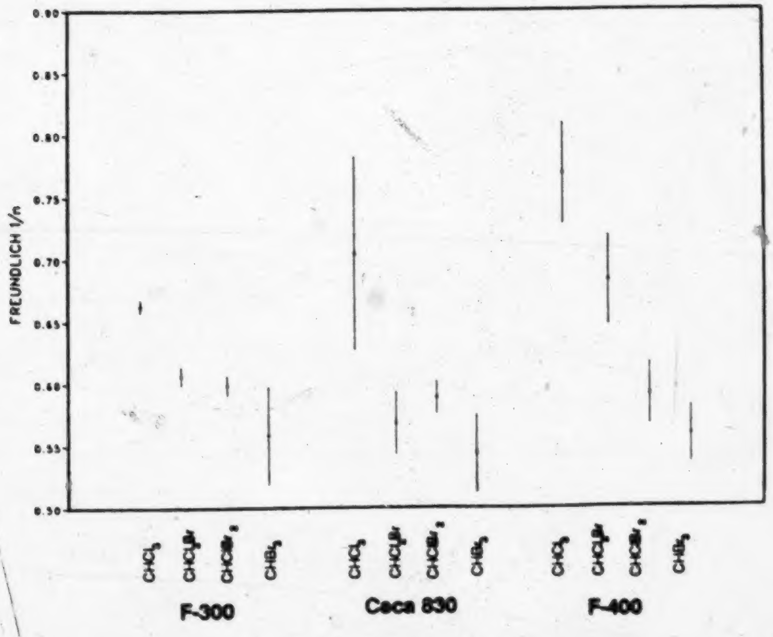


Figure 5.9 Summary of Freundlich 1/n Parameters for Carbons Used in the Study

adsorption parameters obtained for each component (Randtke and Prausnitz, 1972). Luft (1984) has shown that when the Freundlich isotherm equation is used to represent single solute behavior that IAST may be described by equation 2-6, shown previously as:

$$C_i = z_i \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} \qquad i = 1,N \qquad (2\text{-}6)$$

Where: C_i = equilibrium solution concentration

z_i = mole fraction of component i adsorbed on the carbon surface

N = number of components in mixture

n_i = inverse of the Freundlich parameter 1/n for component i

q_i = single solute solid phase concentration for component i

K_i = Freundlich capacity parameter K for component i

Equation 2-6 may then be combined with an equilibrium mass balance equation such that the liquid phase concentration may be eliminated. As a result of this simplification, IAST may be used to calculate the values of q_i and C_i in multicomponent mixtures. For this purpose, only the single solute isotherm parameters and initial concentrations need be known for each component and values for bottle volume and carbon dosages be specified.

To verify that IAST could be used to predict equilibrium behaviour in known mixtures at low concentration levels of THM's (less than 100 µg/L) a series of experiments involving both two and four component mixtures was designed. Two component mixtures were composed of chloroform and bromodichloromethane. Four component mixtures included the adsorbates of the two component mixture plus the more strongly adsorbing components, dibromochloromethane and bromoform. In all cases an initial concentration of 2 µM/L of each component was spiked into organic free (Milli-Q®) water prior to filling individual isotherm bottles.

Multicomponent isotherm results, IAST predictions, and single solute data for individual components of the two and four component mixtures are discussed in Sections 5.4.1 to 5.4.3 for the three carbons tested. For the figures shown in these sections, single solute data obtained in organic free water are represented by a broken line. The adsorptive strength of an individual component in the mixture may be noted by comparing the experimental data and associated IAST prediction to the single solute line.

5.4.1 Filtrasorb 300® Carbon

The first application to verify IAST at low THM concentrations was to predict multicomponent equilibria using the F-300 carbon. As input, the program required Freundlich isotherm parameters, carbon dosages, and initial concentrations for each component. The computer program is shown in Appendix IV.

Typical plots showing a comparison of IAST predictions to experimentally obtained data are presented for two component and four component mixtures in Figures 5.10 to 5.11 and 5.12 to 5.15, respectively. The two component isotherm experiments involved the use of a weakly adsorbing component (chloroform) and a moderately adsorbing component (bromodichloromethane) as denoted by their relative adsorptive capacity (K) values and displacements of multicomponent data from the single solute (Milli-Q® water) isotherm line. Initial spiked concentrations of chloroform and bromodichloromethane were 2 μM/L each. In both cases IAST predictions compared well to experimentally obtained data points although the IAST predictions slightly underestimated competitive displacement.

Competitive displacement was even more evident in the four component isotherm plots. These isotherm experiments involved the two previously mentioned compounds plus dibromochloromethane and bromoform, each spiked at an initial concentration of 2 μM/L. Both the displacement and curvature of the isotherm line were smaller for the more strongly adsorbing compounds. A large displacement for chloroform from the single solute line was observed in the region of high liquid phase concentrations where other components compete more effectively for the limited adsorption sites present when using small carbon dosages. Similar observations were reported by Frick and Sontheimer (1983) for two and three component mixtures.

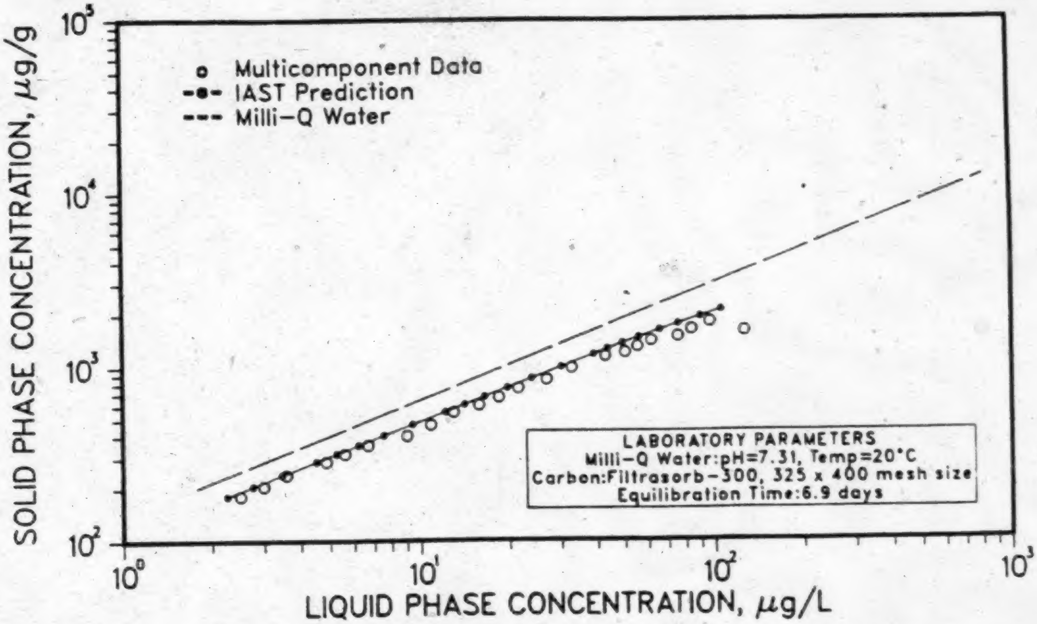


Figure 5.10 Comparison of IAST Prediction to Experimental Data for Chloroform in a Two Component Mixture

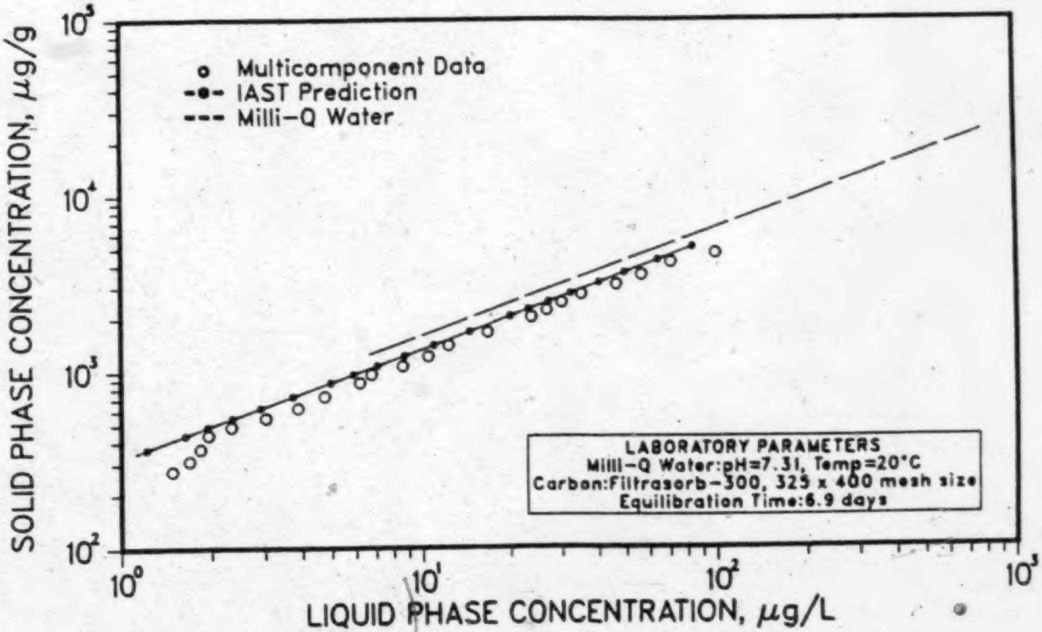


Figure 5.11 Comparison of IAST Prediction to Experimental Data for Bromodichloromethane in a Two Component Mixture

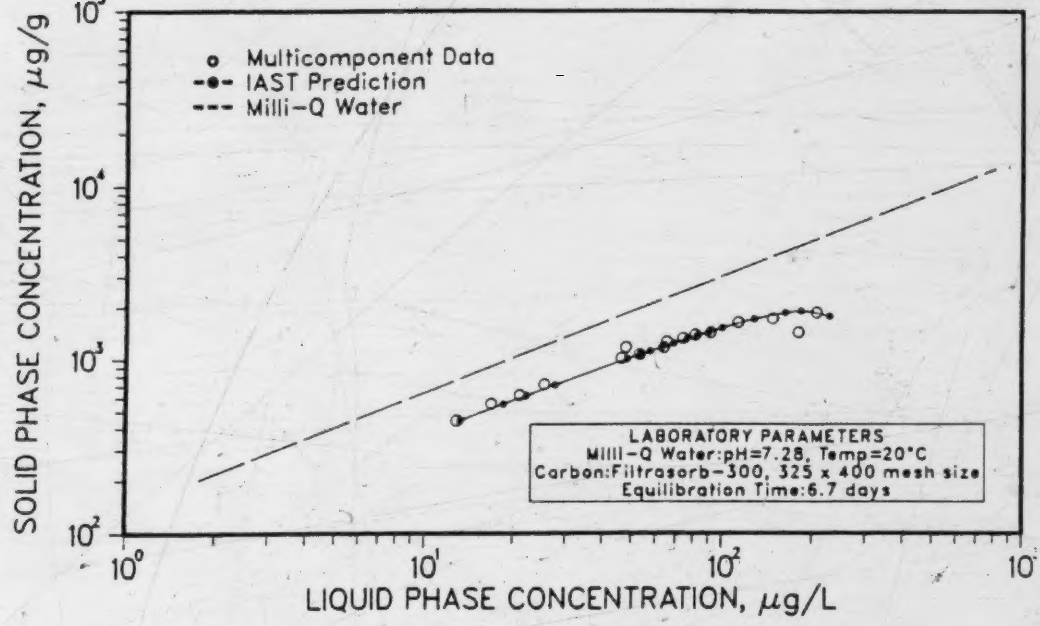


Figure 5.12 Comparison of IAST Prediction to Experimental Data for Chloroform in a Four Component Mixture

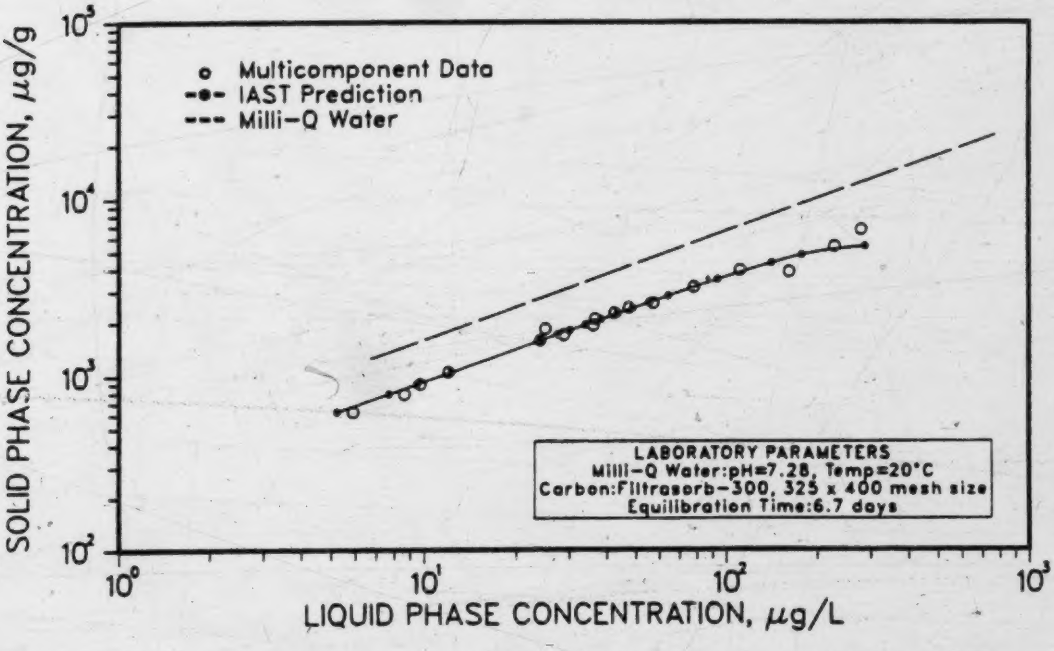


Figure 5.13 Comparison of IAST Prediction to Experimental Data for Bromodichloromethane in a Four Component Mixture

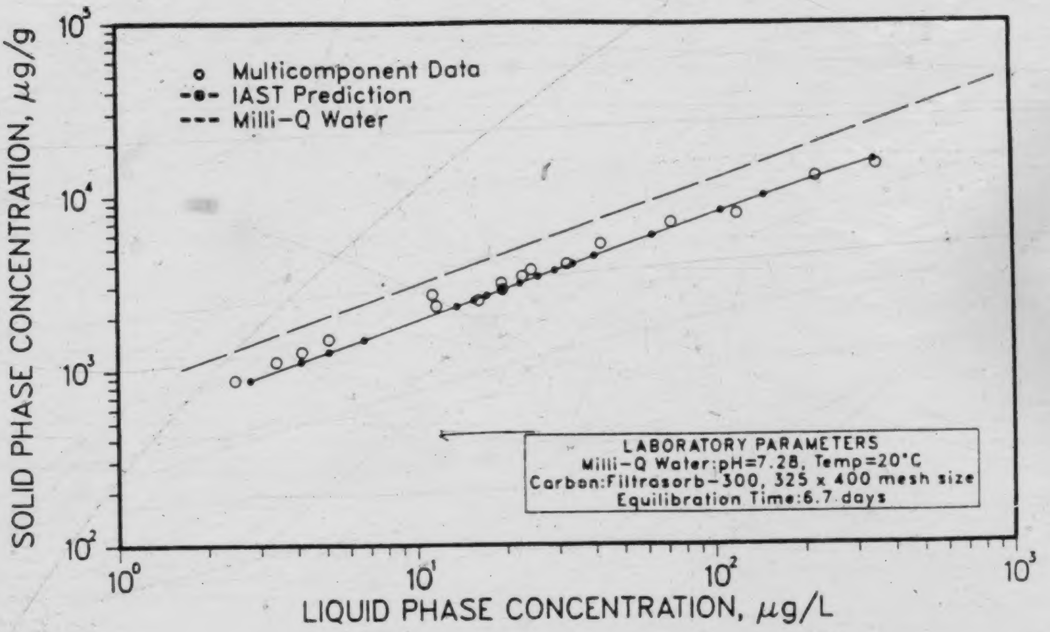


Figure 5.14 Comparison of IAST Prediction to Experimental Data for Dibromochloromethane in a Four Component Mixture

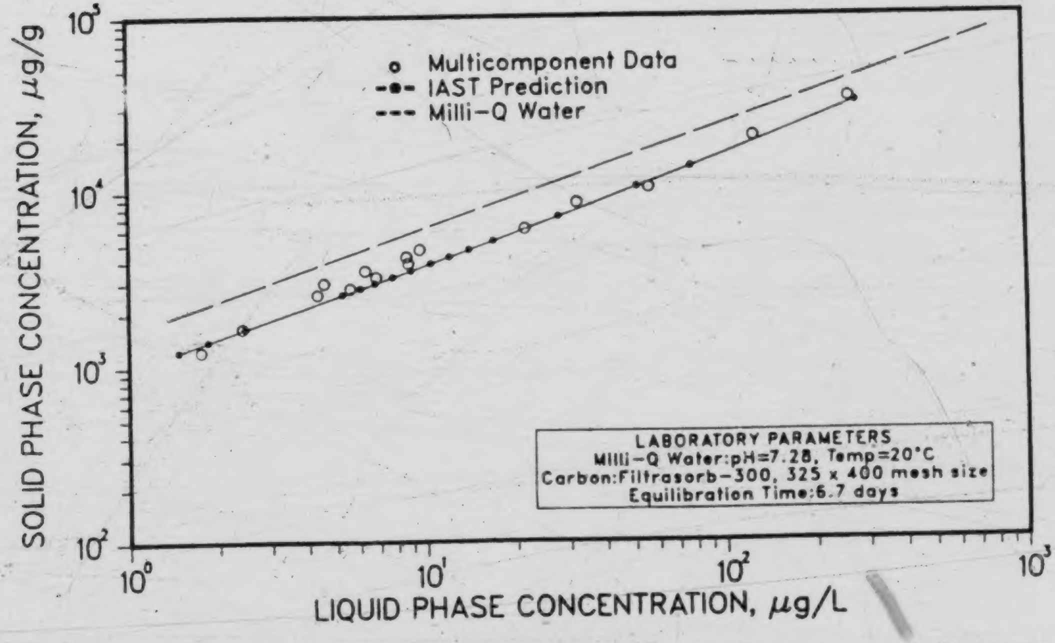


Figure 5.15 Comparison of IAST Prediction to Experimental Data for Bromoform in a Four Component Mixture

5.4.2 Ceca 830 Carbon

Two and four component IAST predictions based on Freundlich parameters are shown in Appendix V (Figures V.1 to V.6). For the two component cases IAST tended to overestimate overall competitive displacement, especially at concentrations less than 100 µg/L. This problem may have been due in part to the extrapolation of single solute data during calculations using IAST to equilibrium loading values much above and below those actually measured in the laboratory. Similar prediction discrepancies were reported by Luft (1984) for weakly adsorbing components. A detailed discussion of this topic is presented in Section 5.4.4.

Predictions for bromodichloromethane in a two component mixture tended to underestimate overall displacement, especially at equilibrium concentrations less than 20 µg/L.

IAST predictions of competitive displacement for the four component mixture in general followed the same trend as reported for the F-300 carbon. Both overall competitive displacement and isotherm curvature decreased as the adsorptive strength of an individual component increased. Very good fits of predicted to experimental data were shown for bromodichloromethane, dibromochloromethane and bromoform. The lack of fit evident for the chloroform prediction was most likely due to the problem mentioned earlier.

5.4.3 Filtrasorb 400® Carbon

Results comparing IAST predictions to experimental data for two and four component mixtures using F-400 are shown in Appendix

V (Figures V.7 to V.12). In general, predictions simulated observed competition for both chloroform and bromodichloromethane in the two component mixture. The apparent lack of fit evident at high liquid phase concentrations (low carbon dosages) was most likely due to variations in experimental data rather than predictive inadequacies since more scatter in the data was evident.

Predictions for the four component mixture provided very good fits to experimental data for the strongly adsorbing components dibromochloromethane and bromoform. IAST however did not predict competitive displacement well for chloroform or bromodichloromethane, especially at equilibrium concentrations less than 100 µg/L.

5.4.4 Estimation of Spreading Pressure

In a similar approach to that described by Luft (1984) and Crittenden et al. (1985b), an analysis of spreading pressure (surface tension) was used to assess the quality of fit of IAST predictions to experimental data. Spreading pressure for a particular solute may be defined as the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface (Singer and Yen, 1980). Using the Freundlich equation to evaluate spreading pressure it was sometimes necessary to extrapolate single solute isotherm data above and below actual laboratory data especially for weakly adsorbing mixture components. Equation 5-1 shown below was used in IAST to equate the spreading pressure of single components to the spreading pressure of the mixture.

$$\frac{\pi_i^o A}{RT} = \int_o^{q_i^o} \frac{d(\ln C_i^o)}{d(\ln q_i^o)}\, dq \qquad (5\text{-}1)$$

where: C_i^o = single solute liquid phase concentration for component i at the spreading pressure of the mixture

q_i^o = single solute solid phase concentration for component i at the spreading pressure of the mixture

π_i^o = single solute spreading pressure of solute i

A = cross sectional area

R = universal gas constant

T = temperature

q = solid phase concentration

The range of extrapolated data above and below single solute data used in spreading pressure calculations may be analyzed graphically by plotting:

$$\frac{d(\ln C_i^o)}{d(\ln q_i^o)} \;\underline{vs}\; q_i^o \qquad (5\text{-}2)$$

As an example, Figure 5.16 shows the spreading pressure evaluation for individual components in a four component mixture on Ceca 830. In this case the range of single solute data actually measured (the region enclosed in square brackets) was adequately covered for bromoform and dibromochloromethane. For bromodichloromethane and chloroform single solute data was

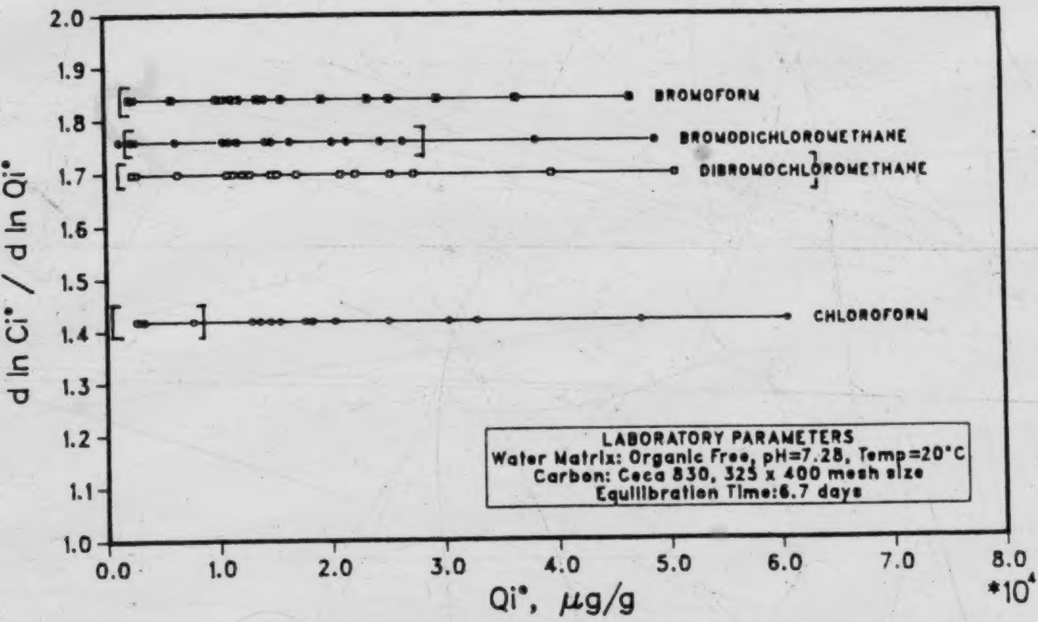


Figure 5.16 Spreading Pressure Evaluation with Single Solute Surface Loadings: Four Component Mixture

(Note: For bromoform, the range of measured single solute data was off-scale therefore no right hand bracket appears.)

extrapolated slightly above and greatly above measured data respectively. As mentioned in Section 5.4.2 the lack of fit evident for the chloroform prediction was most likely due to the large extrapolation of single solute data in IAST calculations.

5.4.5 Comparison Among Carbons

For the three carbons evaluated (F-300, Ceca 830, F-400) IAST was successfully used to predict multicomponent adsorption in known THM mixtures. In most cases, however, prediction of the weakly adsorbing component, chloroform, was less accurate than for the others.

Predicted data for four component mixtures was found to more closely approximate experimental results than in the weaker adsorbing two component cases. This may partially be attributed to the similarity in adsorptive capacity for the components used in the two component mixture. Isotherm curvature noted for weakly adsorbing compounds at high liquid phase concentrations (low carbon dosages) is a direct result of highly competitive (strongly adsorbing) compounds which cause a reduction in the number of available adsorption sites.

Predictions which approximated experimental data were obtained for the F-300 and Ceca 830 carbons. This was important since these are the two carbons used in the GAC contactors at the Buffalo Pound water treatment plant. Also, typically all four THM components are present in the actual pre-GAC treatment plant water. The obtaining of valid predictions at individual component concentration levels simulating treatment plant concentrations (i.e.

< 100 µg/L) was considered important as a first step in the application of computer simulation models since IAST was used as a subroutine in all other models employed.

5.5 Application of the Hypothetical Component Fitting Program (HCFP)

The degree to which specific organic compounds are adsorbed on GAC is dependent on the competitive interactions of both known and unidentified or background organics present in the background matrix (Frick and Sontheimer 1983, Crittenden et al., 1984a, Crittenden et al., 1985b). For adsorption equilibrium purposes, competitive interactions attributable to background organics may be represented by one or more hypothetical components (HC's), (Luft, 1984). The HC parameters (Freundlich K and 1/n, and initial concentration C_{io}) may be determined by measuring the adsorption of a weakly adsorbing tracer compound which is either added to the background matrix or already present in the mixture. HC parameters represent the competitive strength of all unidentified components in the mixture (Crittenden et al., 1984b), and may be used in conjunction with single solute isotherm parameters for a given compound (i.e. THM component) to predict competitive adsorption equilibria for that compound in the unknown background matrix. The HC parameters are generated from the experimental data using the Hypothetical Component Fitting Program (HCFP, Appendix IV) (Speth, 1986), which is essentially a parameter search routine. HC parameters serve as input to the IAST program in addition to the single solute parameters for the compound to be studied. Therefore, the competitive adsorption interactions attributable to an unknown background matrix may be predicted for any specific compound in that matrix. Predicted isotherms may then be compared to experimental observations to verify the model adequacy.

The foregoing discussion describes the "state-of-the-art" at the start of the research and accounts for the simultaneous adsorption of background organics and the compound of interest. During the conduct of the research new information became available regarding the gradual reduction in carbon capacity in full-scale contactors due to slow diffusion of high molecular weight background organics. This new information necessitated implementation of the pre-loading approach described in Section 5.6.

To assist in evaluating prediction accuracy, an equation which computes average percentage error (APE) when estimating IAST fits of predicted to observed data was incorporated into the IAST program. The equation shown below was used to estimate APE's when comparing IAST predicted values of C_i and q_i to those determined experimentally.

$$\mathrm{APE} = \frac{100}{N} \sum \frac{|\text{Observed Value - Predicted Value}|}{\text{Observed Value}} \qquad (5\text{-}3)$$

Where: N = number of data points.

Division by the observed (experimental) value normalizes the error and allows APE's for compounds of varying adsorptive strengths to be directly compared. Such a direct comparison would be impossible with the more usual residual sum of squares approach.

5.5.1 Determination of Hypothetical Components for a Known Trihalomethane Mixture

As an initial assessment of model adequacy, the HCFP was used to estimate background competition in a four component pure water isotherm on F-400. Chloroform was selected as the background matrix tracer component. From prior single solute isotherm analyses (comparison of Freundlich K's) it was determined that chloroform did not comprise a significant portion of the adsorbing components in the mixture.

IAST predictions using an HC fit to a chloroform tracer are shown in Figures 5.17 to 5.20. The APE's for the four predictions are shown in Table 5.3. In general, values for equilibrium capacity (Q) were predicted more accurately than equilibrium concentration (C) especially for the more weakly adsorbing components such as chloroform and bromodichloromethane.

5.5.2 Prediction of Multicomponent Equilibria in Unknown Background Matrices

Isotherm experiments were designed and conducted to assess competition in unknown background matrices. Chlorinated influent water to the GAC contactors at Buffalo Pound, collected at four different periods during the 1986 summer-fall operating season was used for this purpose. Isotherm plots for Ceca 830, Filtrasorb 300®, and Filtrasorb 400® were prepared (Appendix V). In each case concentrations of the four trihalomethane components were spiked by the addition of 2 μM/L such that equilibrated residual concentrations could be easily measured using gas chromatography.

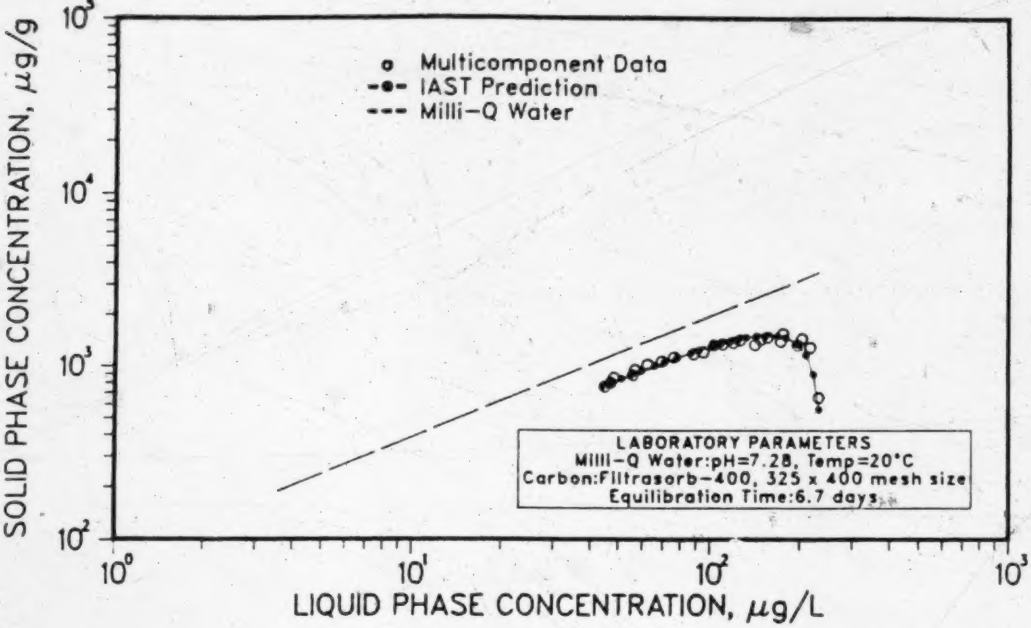


Figure 5.17 IAST Predictions for Chloroform in a Four Component Mixture Using HC's Fit to Chloroform

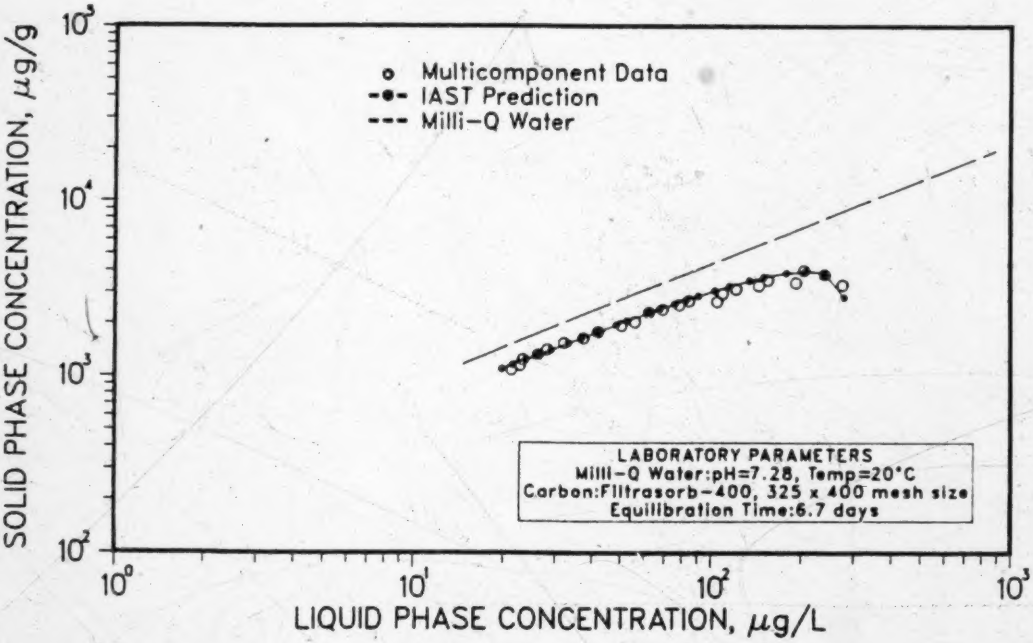


Figure 5.18 IAST Predictions for Bromodichloromethane in a Four Component Mixture Using HC's Fit to Chloroform

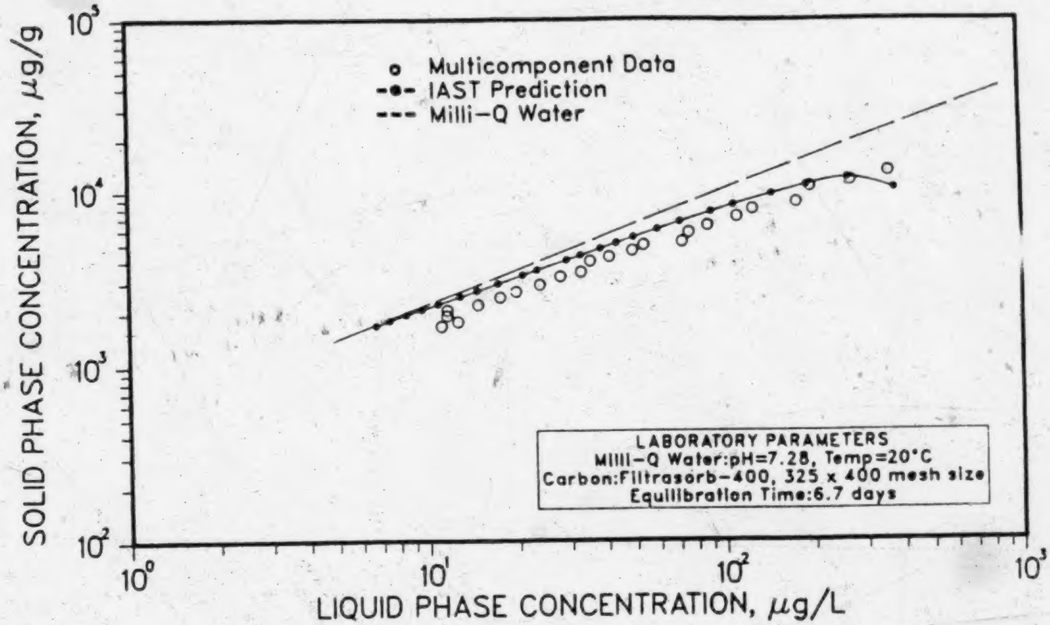


Figure 5.19 IAST Predictions for Dibromochloromethane in a Four Component Mixture Using HC's Fit to Chloroform

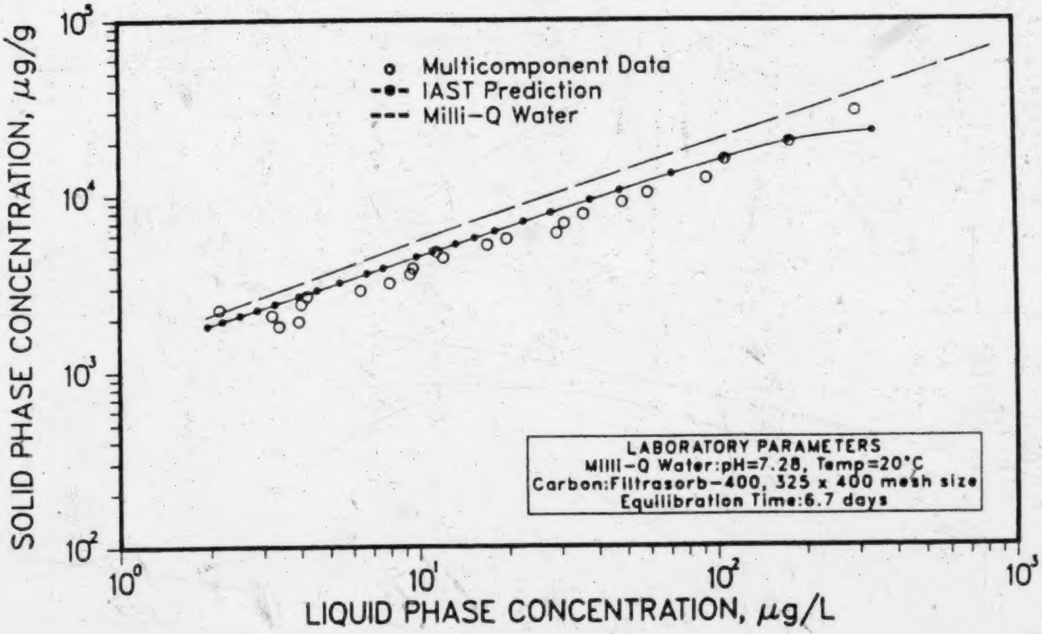


Figure 5.20 IAST Predictions for Bromoform in a Four Component Mixture Using HC's Fit to Chloroform

Table 5.3 Hypothetical Component Properties and Resulting APE's for a Four Component Mixture on Filtrasorb 300®

Compound	Fit/Predicted	APE (%)	
		C	Q
Chloroform	Fit		
Chloroform	Predicted	3.04	7.12
Bromodichloromethane	Predicted	3.81	2.80
Dibromochloromethane	Predicted	21.6	3.83
Bromoform	Predicted	22.3	2.11

Hypothetical Component Properties:

$K(\mu M/g)(L/\mu M)^{1/n}$	1/n	C_o (μM/L)
808.15	0.400	0.7420

The purpose of collecting this data was to determine the background matrix strength, including any changes which occurred during the 1986 GAC operating period. The background matrix strength could then be represented by hypothetical components (HC's) using the Hypothetical Component Fitting Program (HCFP).

Initially both chloroform and bromodichloromethane were evaluated as potential candidates to serve as background matrix tracer components. Subsequent IAST predictions showed that HC's generated from the bromodichloromethane tracer produced a better fit of predicted to observed data. In general, average percentage error (APE) values for both C and Q were lower when bromodichloromethane was used as the tracer. For each of the four different Buffalo Pound water matrices a unique set of HC's was generated. Each set of HC's included values for the Freundlich parameters K and 1/n and an initial concentration C_o. It should be noted that where HC's are concerned, both K and C_o are given in terms of micromoles instead of the more commonly used microgram units. In generating HC's, the value for 1/n was fixed at 0.4 on the recommendation of Dr. John Crittenden (1986). This resulted in the program having to search for only two parameters (K and C_o) thus greatly reducing computation time. In general, initial approximations for K and C_o were set at 800.0 and 8.0, respectively. Program convergence was attained when the change in normalized liquid concentration data was less than 0.0001 for two consecutive iterations.

Once HC's were obtained for the four background matrices they were used as input to the IAST program which predicted isotherm displacement due to background competition. An APE was calculated for each fit of predicted to observed data.

5.5.2.1 Filtrasorb 300® Carbon

IAST predictions for the four components are presented for one background matrix in Figures 5.21 to 5.24. A full set of all plots are included in Appendix V. HC estimates and APE's for each THM component in four different background matrices are reported for the F-300 carbon in Tables 5.4 and 5.5. In all cases the APE's for the predicted components are very low indicating that the model could satisfactorily predict values comparable to those determined experimentally.

5.5.2.2 Ceca 830 Carbon

IAST predictions using HC's for Ceca 830 carbon are shown in Appendix V. HC estimates and APE's for individual water matrices are reported in Tables 5.6 and 5.7. The predictions closely approximated experimental data as evidenced by the low APE's, especially for solid phase loading values (Q).

5.5.3 Prediction of Multicomponent Equilibria Using Averaged Hypothetical Component Values

As part of investigations which assessed the general applicability of using HC's, an attempt was made to predict isotherm displacement for the four different water matrices by using averaged HC values to represent the complete operating period. A successful application of this approach would show that small

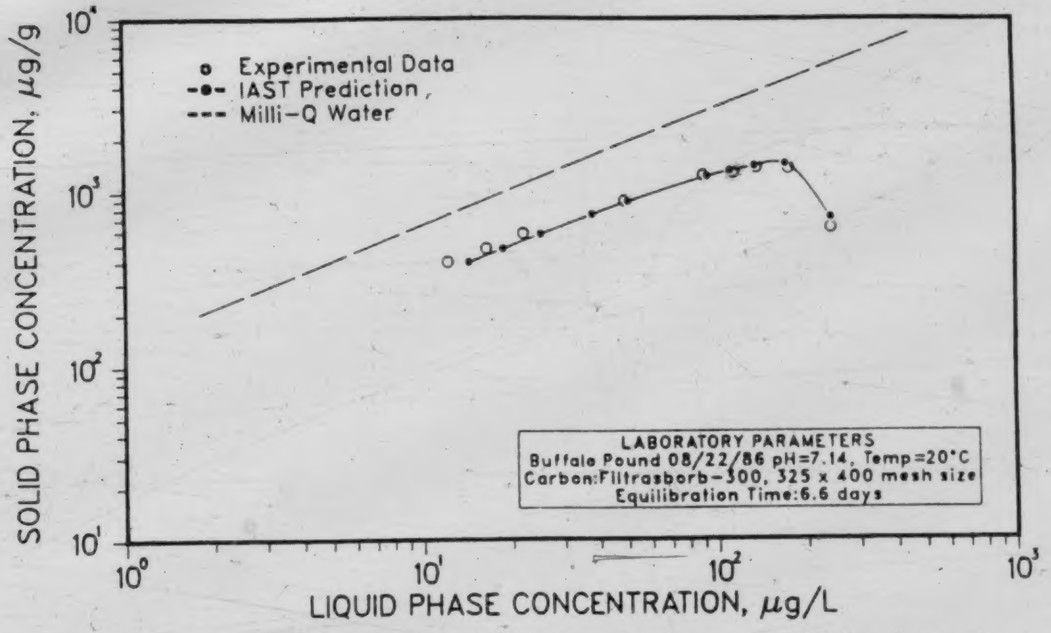


Figure 5.21 IAST Prediction for Chloroform on F-300 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

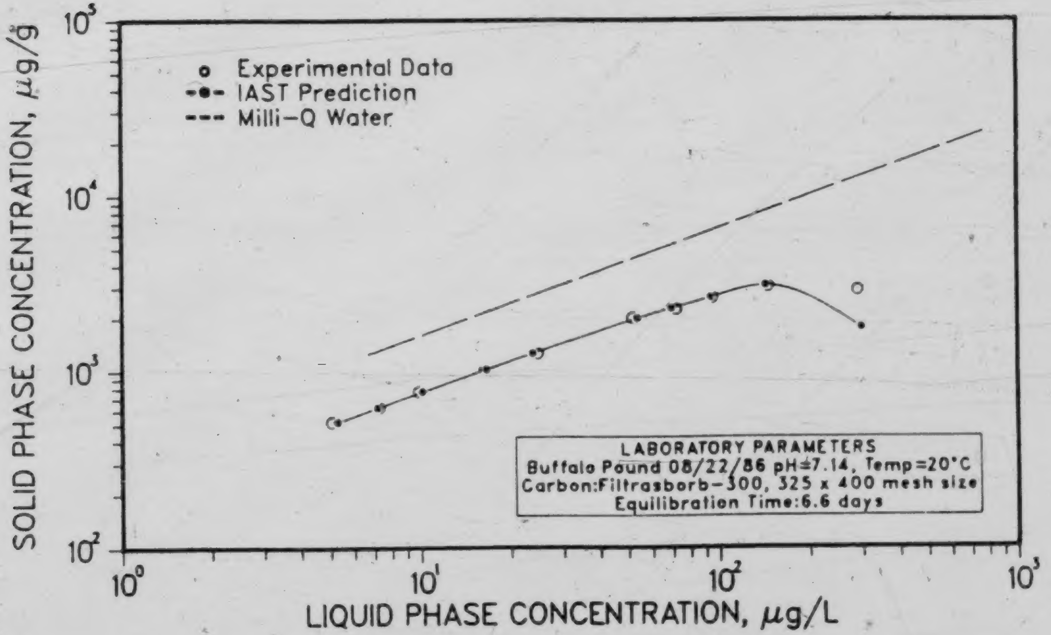


Figure 5.22 IAST Prediction for Bromodichloromethane on F-300 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

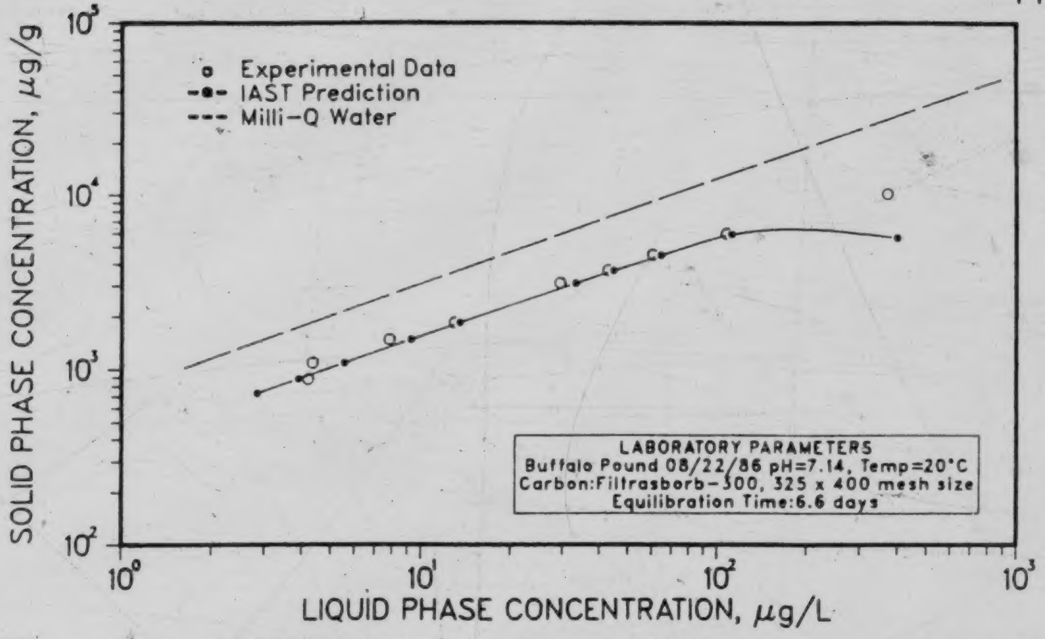


Figure 5.23 IAST Prediction for Dibromochloromethane on F-300 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

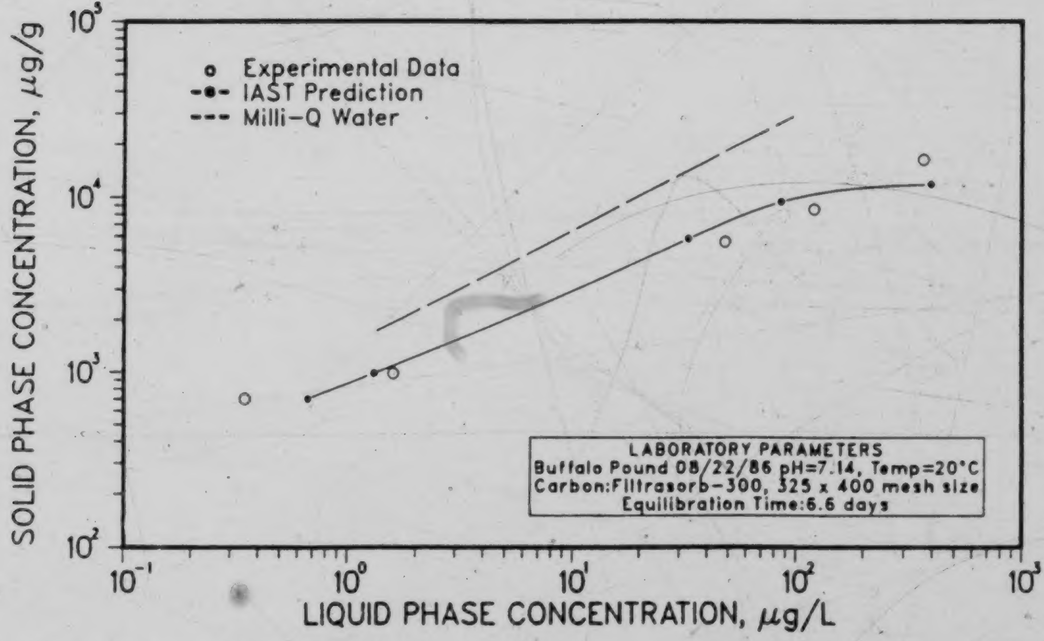


Figure 5.24 IAST Prediction for Bromoform on F-300 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

Table 5.4 Hypothetical Component Properties for Four Water Matrices on F-300 Carbon

Hypothetical Component Properties[a]	Water Matrix Collection Date 08/22/86	09/22/86	10/06/86	10/22/86
K $(\mu M/g)(L/\mu M)^{1/n}$	784	810	263	797
C_o $(\mu M/L)$	4.03	3.28	3.85	4.07

[a] 1/n fixed at 0.400

Table 5.5 Resulting APE's for Four Water Matrices on F-300 Carbon

a. APE (%) for Q

Compound	Water Matrix Collection Date			
	08/22/86	09/22/86	10/06/86	10/22/86
Chloroform	3.07	13.5	6.27	0.93
Bromodichloromethane	4.42	1.99	4.74	0.28
Dibromochloromethane	4.91	1.43	4.22	NC
Bromoform	8.34	NC	NC	NC

NC - Not Calculated

b. APE (%) for C

Compound	Water Matrix Collection Date			
	08/22/86	09/22/86	10/06/86	10/22/86
Chloroform	5.73	28.5	7.27	10.7
Bromodichloromethane	2.65	4.89	3.64	5.98
Dibromochloromethane	40.4	21.5	16.5	NC
Bromoform	35.3	NC	NC	NC

NC - Not Calculated

Table 5.6 Hypothetical Component Properties for Four Water Matrices on Ceca 830 Carbon

Hypothetical Component Properties[a]	Water Matrix Collection Date			
	08/22/86	09/22/86	10/06/86	10/22/86
K $(\mu M/g)(L/\mu M)^{1/n}$	793	808	792	796
C_o $(\mu M/L)$	3.57	3.81	4.45	4.27

[a] 1/n fixed at 0.400

Table 5.7 Resulting APE's for Four Water Matrices on Ceca 830 Carbon

a. APE (%) for Q

Compound	Water Matrix Collection Date			
	08/22/86	09/22/86	10/06/86	10/22/86
Chloroform	6.59	6.62	9.41	40.1
Bromodichloromethane	9.23	0.49	6.61	0.75
Dibromochloromethane	10.8	0.65	5.31	0.28
Bromoform	10.3	0.66	4.29	NC

NC - Not Calculated

b. APE (%) for C

Compound	Water Matrix Collection Date			
	08/22/86	09/22/86	10/06/86	10/22/86
Chloroform	25.3	23.0	15.4	29.4
Bromodichloromethane	7.37	2.15	2.05	14.1
Dibromochloromethane	17.3	9.39	10.5	7.10
Bromoform	32.4	11.3	13.1	NC

NC - Not Calculated

changes in the background matrix would not significantly influence predictions concerning specific compound adsorption during actual GAC contactor operation.

IAST predictions for Ceca 830 carbon using the mean of four HC's fit to bromodichloromethane are shown in Figures 5.25 to 5.28. Predictions are compared to experimental data for the August 22 water matrix. A complete set of plots for other water matrices is included in Appendix V. The Ceca 830 carbon was chosen for this exercise since it was the carbon used in most of the GAC adsorbers at Buffalo Pound. The HC's used for each specific water matrix were obtained by taking the average of the four previously determined K and C_0 values. An average was not taken for 1/n since in all cases this was set to 0.4 when predicting HC's. APE's based upon predictions made using both averaged and original (non-averaged) HC's were calculated for each water matrix and are compared in Table 5.8 and Appendix V.

In general, neither APE's for C nor Q were significantly influenced by the use of averaged HC values. For the water matrices of August 22, 1986 (Table 5.8) and June 10, 1986 (Appendix V) predictions using averaged HC's provided improved estimates for Q. In the worst case (September 22, 1986, Appendix V) prediction of Q for dibromochloromethane using averaged HC's resulted in an error increase from 0.65% to 10.5%.

The foregoing analysis suggests that determination of unique HC values is not required to represent background competition for a given time during the full-scale GAC adsorber operation season at Buffalo Pound. The relative adsorbability of any compound of

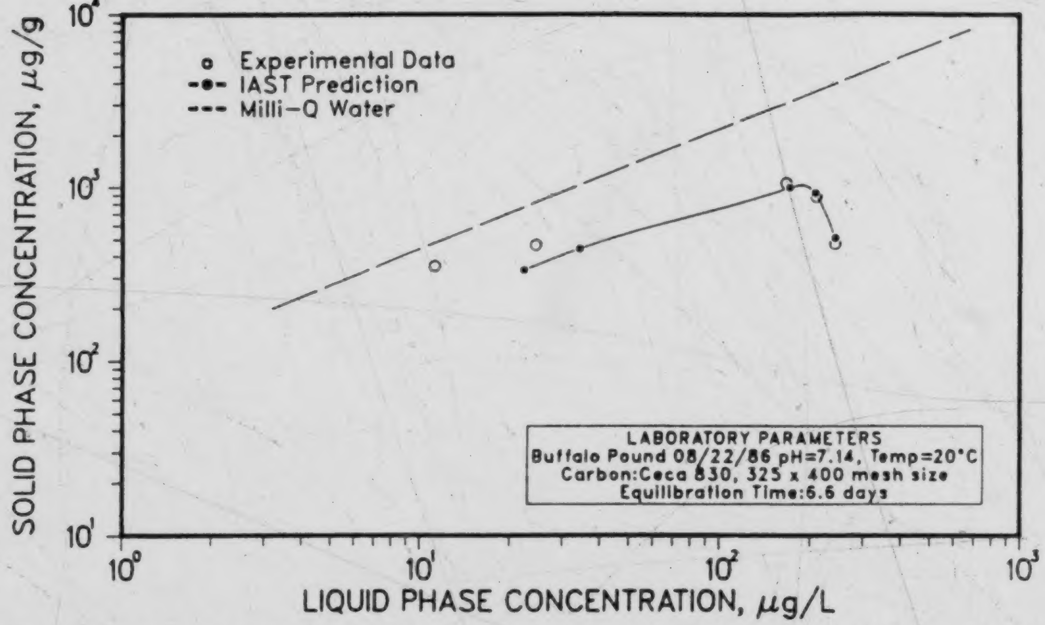


Figure 5.25 IAST Prediction for Chloroform on Ceca 830 Using Mean of HC's Fit to Bromodichloromethane, August 22, 1986 Buffalo Pound Water Matrix

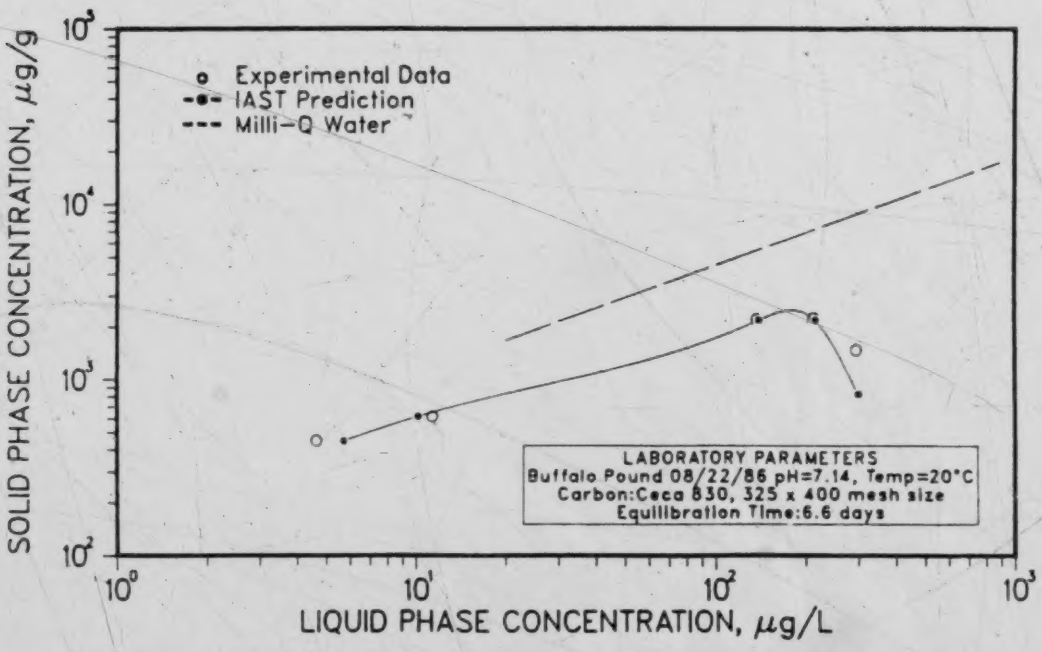


Figure 5.26 IAST Prediction for Bromodichloromethane on Ceca 830 Using Mean of HC's Fit to Bromodichloromethane, August 22, 1986 Buffalo Pound Water Matrix

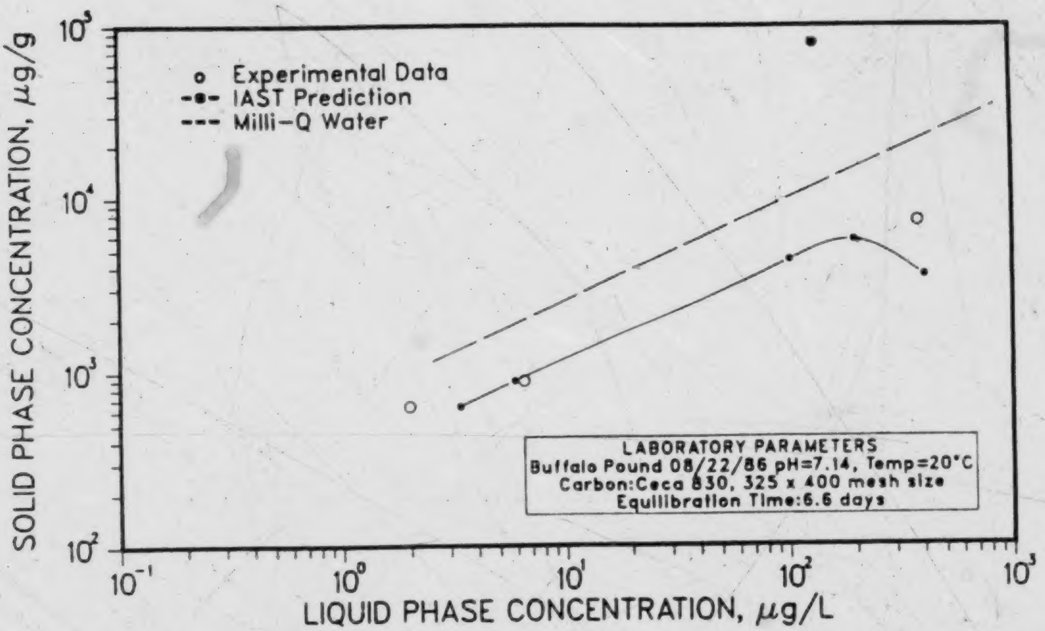


Figure 5.27 IAST Prediction for Dibromochloromethane on Ceca 830 Using Mean of HC's Fit to Bromodichloromethane, August 22, 1986 Buffalo Pound Water Matrix

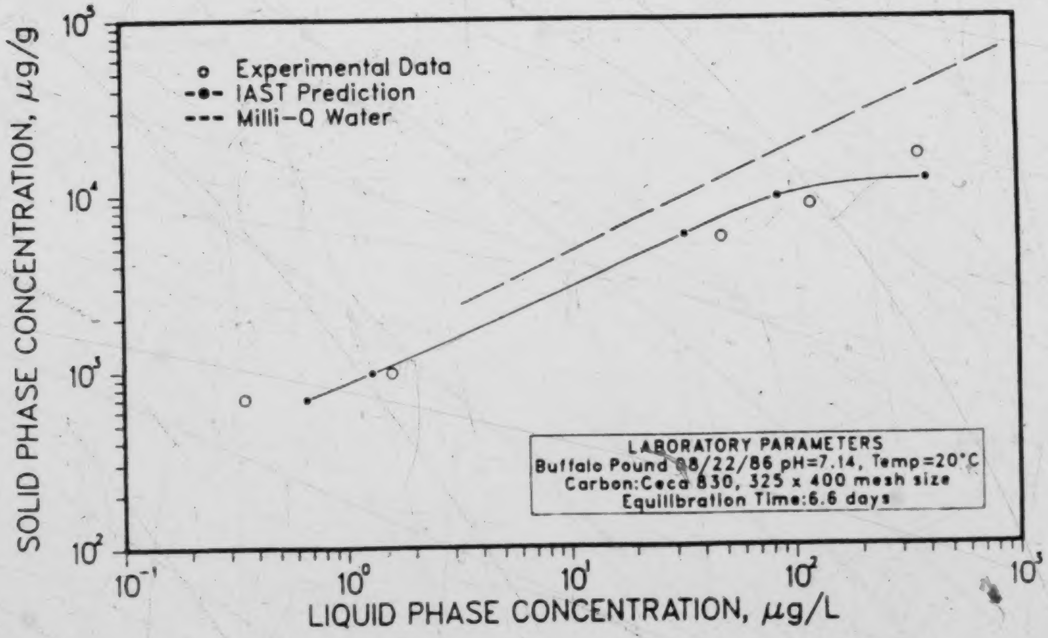


Figure 5.28 IAST Prediction for Bromoform on Ceca 830 Using Mean of HC's Fit to Bromodichloromethane, August 22, 1986 Buffalo Pound Water Matrix

Table 5.8 Comparison of APE's for IAST Using Both Averaged and Non-Averaged HC's - August 22, 1986 Water Matrix on Ceca 830

Hypothetical Component Properties:

	K $(\mu M/g)(L/\mu M)^{1/n}$	1/n	C_o $(\mu M/L)$
Original	793	0.400	3.57
Averaged	797	0.400	4.02

Compound	Fit/Predicted	APE (%)			
		Original HC's		Averaged HC's	
		C	Q	C	Q
Bromodichloromethane	Fit				
Chloroform	Predicted	25.3	6.59	25.3	3.60
Bromodichloromethane	Predicted	7.37	9.23	17.3	0.74
Dibromochloromethane	Predicted	17.3	10.8	7.27	0.61
Bromoform	Predicted	32.4	10.3	NC	NC

NC - Not Calculated

interest may thereby be calculated knowing only its single solute parameter values and an approximate representation of background competition as defined by HC's. However, background competition during a severe algal bloom, or during winter (if the contactors were to be operating then) might not be adequately predicted by this approach.

The following section provides an examination of the sensitivity of IAST predictions to changes in individual HC parameters.

5.5.4 Hypothetical Component Sensitivity Analysis

A sensitivity analysis was conducted on individual HC parameter values (K, 1/n, and C_o) to assess the influence of individual parameter estimates on subsequent isotherm predictions. The water matrix selected for use in this comparison was that of Buffalo Pound pre-GAC water collected September 22, 1986. This matrix displayed the lowest average percentage error values for the four trihalomethane components when using the Ceca 830 carbon. Original HC values were fit to the tracer component bromodichloromethane.

To illustrate the effect of variation in parameter estimates, the HC parameters K, 1/n, and C_o were individually varied by both ±10% or ±50% prior to use as input data to the IAST program. These parameter values are shown in Table 5.9. The effects of HC variation on IAST predictions for chloroform are shown in Figures 5.29 to 5.34. Results for the other three components were generally similar to those for chloroform (Appendix V).

Table 5.9 HC Parameter Values Used in IAST Sensitivity Analysis

Parameter	Initial Value	-10%	+10%	-50%	+50%
K $(\mu M/g)(L/\mu M)^{1/n}$	808	727	888	404	1,210
1/n	0.400	0.360	0.440	0.200	0.600
C_o (μM/L)	3.81	3.43	4.19	1.91	5.72

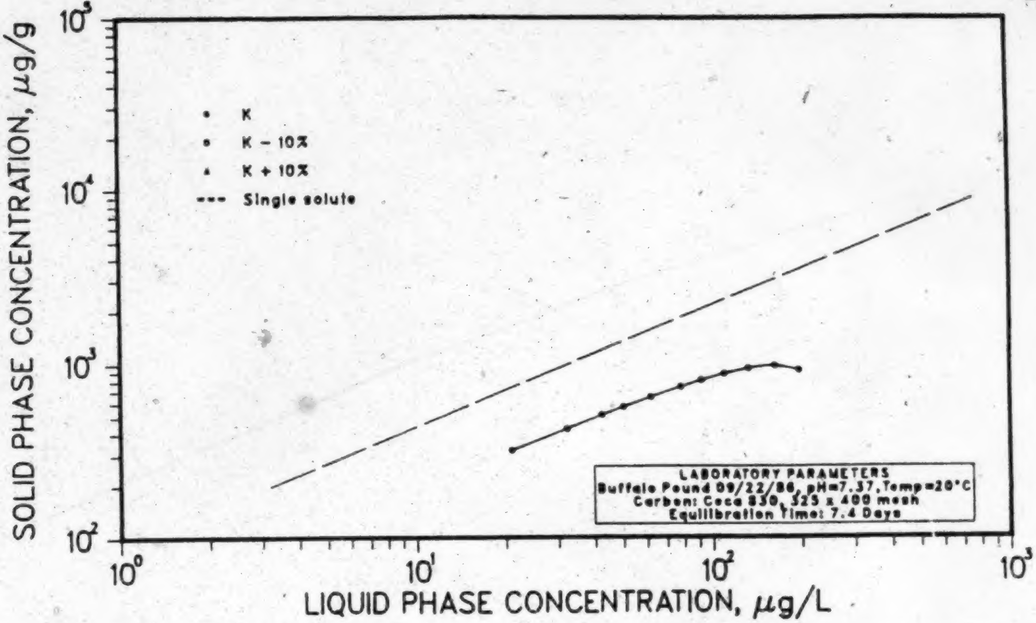


Figure 5.29 Effect of Varying K by 10% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane (Note: Calculated capacities were identical for ±10% change in K)

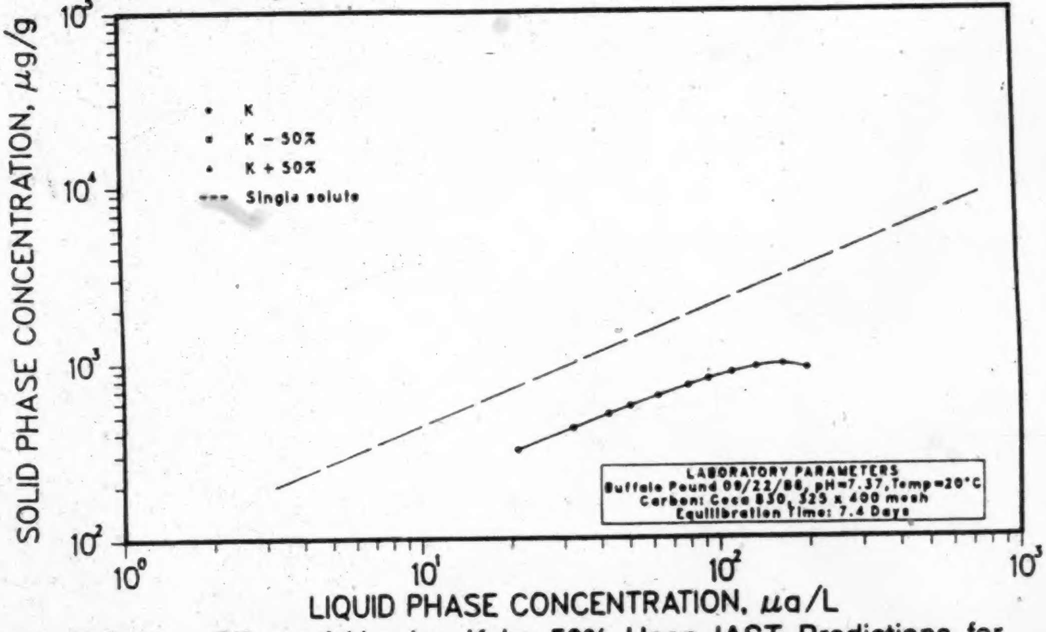


Figure 5.30 Effect of Varying K by 50% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane (Note: Calculated capacities were identical for a ±50% change in K)

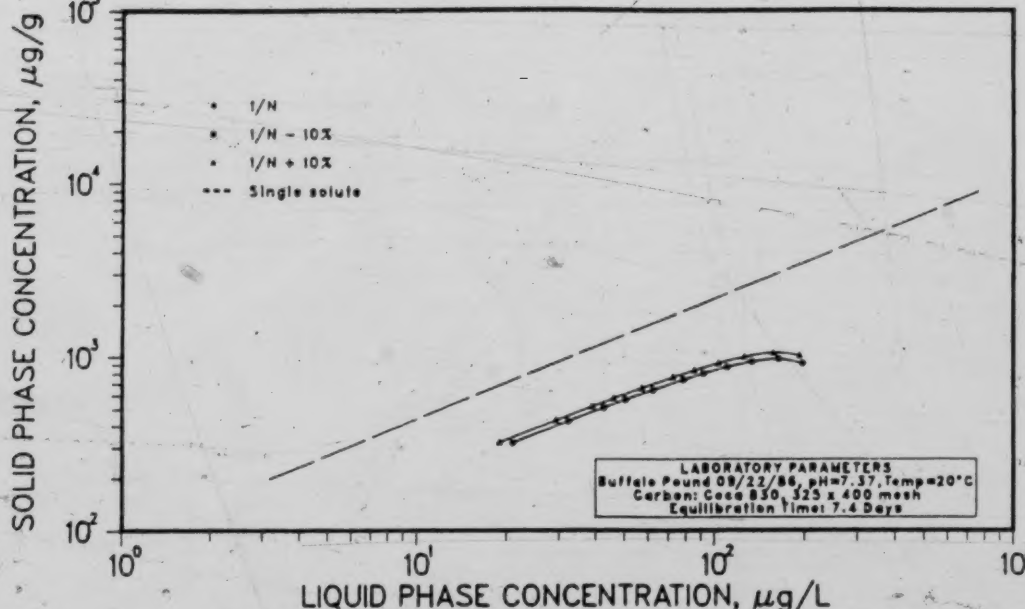


Figure 5.31 Effect of Varying 1/n by 10% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane (Note: Calculated capacities were identical for ±10% change in K)

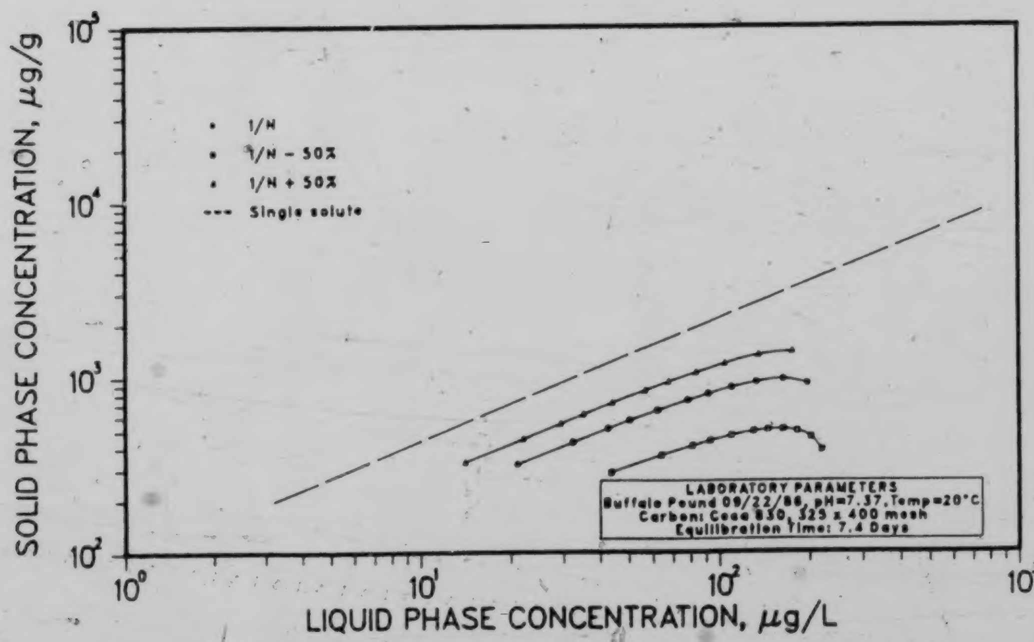


Figure 5.32 Effect of Varying 1/n by 50% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane

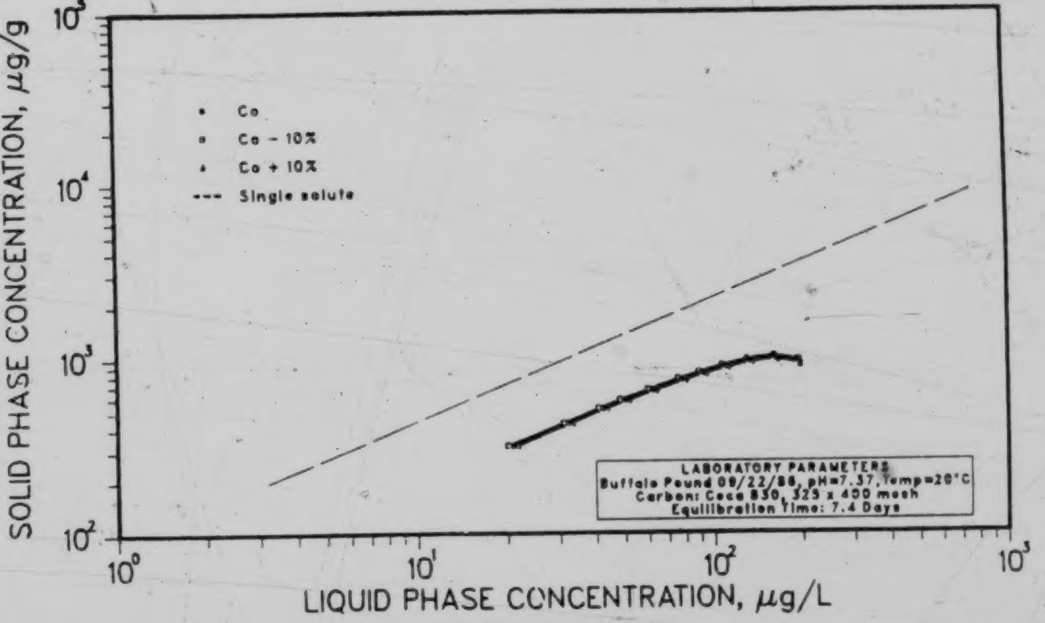


Figure 5.33 Effect of Varying C_0 by 10% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane

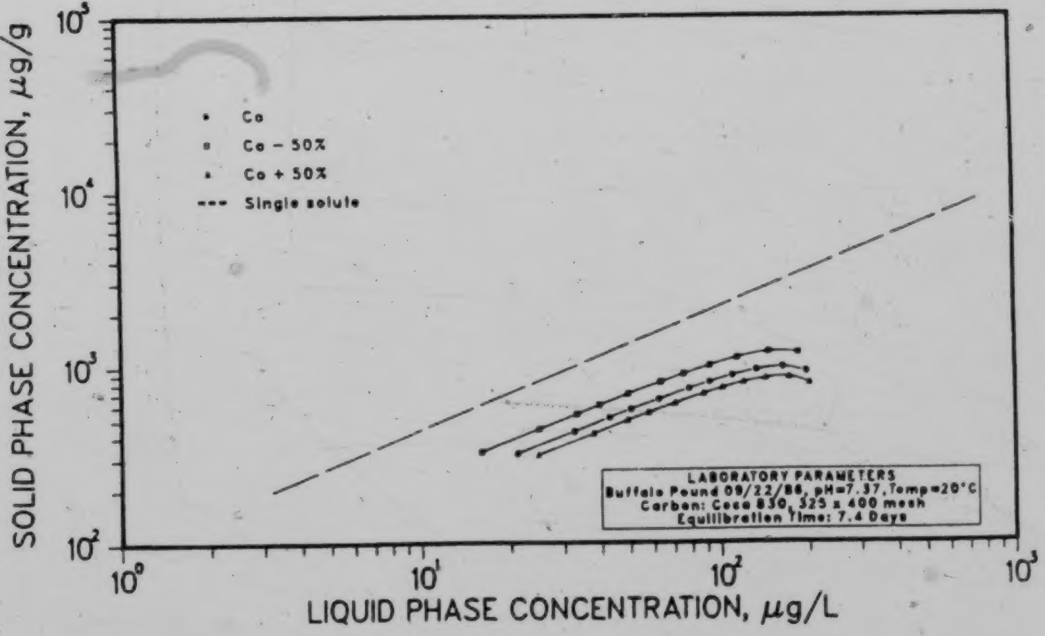


Figure 5.34 Effect of Varying C_0 by 50% Upon IAST Predictions for Chloroform Using HC's Fit to Bromodichloromethane

In general, an increase or decrease in any one of the parameters caused a shift in the predicted isotherm line parallel to itself. To quantify the magnitude of change in adsorptive capacity (Q, μg/g) attributable to a change in an HC parameter, estimates of Q (μg/g) were obtained for an equilibrium concentration of 10 μg/L. These calculated capacities are shown in Appendix V. For the predicted components chloroform, dibromochloromethane, and bromoform, changes in K of up to 50% did not influence the overall capacity. The parameter 1/n displayed the largest influence on adsorptive capacity. Changes in initial concentration, C_o also had an effect on capacity but in most cases this was less significant than a similar change in 1/n.

HC sensitivity results presented in Tables 5.10 to 5.13 show the percentage change in adsorptive capacity as a function of changes in HC's for the four THM components. The results show that a given change in the relative adsorbability of the background as defined by 1/n caused a direct change in predictive adsorptive capacities for a given adsorbate. Changes in the K and C_o of HC's caused capacity to vary inversely.

As observed from the structure of the Freundlich model, the effects of variation in HC parameter estimates on predictions are interrelated. For example, an underestimate in 1/n could be compensated for by an overestimate in C_o.

5.5.4.1 Summary

In modelling work which incorporates IAST emphasis should be placed on the precise estimation of the slope parameter, 1/n. For

Table 5.10 Comparison of Carbon Capacity for Chloroform (Percentage Basis): Hypothetical Components Varied by 10% and 50%

	% Change in Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L			
HC Parameter	-10%	+10%	-50%	+50%
K (μM/g)$(L/\mu M)^{1/n}$	0%	0%	0%	0%
1/n	0%	+2%	-40%	+35%
C_o (μM/L)	+3%	-4%	+20%	-13%

Single Solute Capacity: 403 μg/g (@ C_e = 10 μg/L)

Table 5.11 Comparison of Carbon Capacity for Bromodichloromethane (Percentage Basis): Hypothetical Components Varied by 10% and 50%

	% Change in Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L			
HC Parameter	-10%	+10%	-50%	+50%
K (μM/g)$(L/\mu M)^{1/n}$	0%	0%	+27%	-15%
1/n	-10%	+20%	-21%	+17%
C_o (μM/L)	+4%	-6%	+27%	-15%

Single Solute Capacity: 1312 μg/g (@ C_e = 10 μg/L)

Table 5.12 Comparison of Carbon Capacity for Dibromochloromethane (Percentage Basis): Hypothetical Components Varied by 10% and 50%

	% Change in Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L			
HC Parameter	-10%	+10%	-50%	+50%
K $(\mu M/g)(L/\mu M)^{1/n}$	0%	0%	0%	0%
1/n	-10%	+11%	-57%	32%
C_o (μM/L)	+2%	-6%	+22%	-16%

Single Solute Capacity: 2495 μg/g (@ C_e = 10 μg/L)

Table 5.13 Comparison of Carbon Capacity for Bromoform (Percentage Basis): Hypothetical Components Varied by 10% and 50%

	% Change in Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L			
HC Parameter	-10%	+10%	-50%	+50%
K $(\mu M/g)(L/\mu M)^{1/n}$	0%	0%	0%	0%
1/n	-5%	+7%	-41%	+38%
C_o (μM/L)	+11%	-3%	+33%	-11%

Single Solute Capacity: 5572 μg/g (@ C_e = 10 μg/L)

this purpose isotherm experiments could be designed to minimize the joint confidence region between the K and 1/n parameters. To accomplish this would require controlling the independent variable C_e by judicious selection of carbon dosages.

From a practical application standpoint this numerical evaluation has shown that once K, 1/n, and C_o HC's have been defined for a particular water matrix, changes in initial estimates of C_o and K up to 50% should not significantly influence adsorptive capacity predictions. For the Buffalo Pound water treatment plant capacity predictions for the summer operating period could likely be based on a single isotherm analysis for each compound and carbon of interest since it has been shown that the effect on adsorption of the background matrix changes only very slightly during this period. However, since a major algae bloom was not experienced during 1986, the effect of such an event (while likely short lived) could not be evaluated.

5.6 Estimation of Trihalomethane Capacity Reduction Attributable to Pre-Loading with Background Organics

In column or bed type operations, Baldauf and Zimmer (1986) have shown that the total amount of a particular halogenated organic compound adsorbed at saturation was significantly reduced in the presence of naturally occurring humic substances.

Zimmer et al. (1987a) showed experimentally that the adsorptive capacity of carbon as represented by the Freundlich K for a particular compound decreases with the length of time that the carbon has been "pre-loaded" with background organics. A possible explanation offered by the authors for this phenomenon was pre-adsorption of humic substances in lower filter depths, thus reducing the capacity for organic micropollutants. They also hypothesized that an enrichment of the better adsorbing humics on the carbon over time would cause a further reduction in micropollutant adsorptive capacity. Isotherm analyses conducted in their study focused predominantly on three chlorinated hydrocarbons: 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. Investigations conducted at the Buffalo Pound water treatment plant have also shown capacity reductions for THM components in lower bed segments (Andrews, 1987).

Some past studies have evaluated the effect of background organics on adsorptive capacity using humic acid solutions (Herzing et al., 1977). However, it was also shown that isotherms conducted in well water containing natural organic compounds could not be compared to those conducted with humic acids since the nature of the organic material differed. Malcolm and MacCarthy (1986) compared seven commercial samples of humic acids to humic and fulvic acids isolated from streams and other natural sources. The authors concluded on the basis of ^{13}C NMR data that the commercial humics were not representative of soil or water humic or fulvic acids and should not be used as analogues of soil and water humic substances.

The foregoing discussion suggests that an adequate evaluation of the adsorptive capacity of activated carbon for compounds such as THM requires the use of actual source water to represent the complex background organic matrix. In addition, the carbon must be pre-loaded with the background organic matter since performance of actual adsorbers cannot be represented by tests involving only coadsorption of the background organics.

To provide pre-loaded carbon for use in capacity estimations using isotherms, a specially designed column was constructed and installed at the Buffalo Pound water treatment plant as described in the Chapter 4. Capacity reductions associated with the "pre-loading" effect could then be used in conjunction with established co-adsorption parameters to estimate the actual capacity of GAC contactors.

5.6.1 Isotherm Results Using Freeze-Dried Virgin Carbon

In order to allow crushing of the carbon and ultimately an appropriate sieve fraction to be obtained for use in isotherms, it was necessary to freeze-dry all pre-loaded carbon such that the moisture content could be reduced. However, prior to conducting isotherms to evaluate adsorptive capacity reductions due to pre-loading, isotherm experiments were designed to assess the effect of freeze-drying. A 200 x 400 mesh sieve fraction was selected for use in these experiments. This fraction contained a slightly larger size carbon particle than the 325 x 400 mesh size typically used in isotherm tests. The wider size range was selected to enable a larger volume of carbon to be obtained from a limited quantity of pre-loaded granular carbon.

Single solute isotherm experiments were conducted to obtain estimates of parameter values for chloroform and bromodichloromethane on freeze-dried virgin F-300. A comparison of these values to those previously obtained using virgin non freeze-dried carbon is shown in Table 5.14. Actual isotherms using freeze-dried carbon appear in Figures 5.35 and 5.36.

The process of freeze-drying carbon prior to use did not appear to significantly alter the adsorptive characteristics. Slope values (1/n) were very similar for both single solute components. The adsorptive capacity as defined by K increased for chloroform and decreased for bromodichloromethane, however neither of these changes are considered significant. Slight changes in K values may be attributed, at least in part, to the range of concentration values used in the comparison experiments.

5.6.2 Apparent Density Analyses of Pre-Loaded Carbon

Apparent density analyses were conducted on both virgin carbon and carbon obtained from GAC beds at Buffalo Pound following 135 days of operation during the summer of 1986. The purpose of conducting these analyses was to assess any effect of freeze-drying upon virgin carbon apparent density, and to measure changes in apparent density attributable to pre-loading. All apparent density analyses are conducted in accordance with AWWA standard B604-74 except where appropriate modifications were required as described in Appendix I.1.

Apparent densities of the virgin GACs did not appear to be significantly influenced by the freeze-drying process (Table 5.15). The F-300 apparent density decreased by 1.1% whereas the Ceca 830 apparent density increased by 1.0% as a result of freeze-drying.

Table 5.14 Single Solute Isotherm Results Obtained Using Freeze-Dried and Non Freeze-Dried F-300 Carbon

Carbon Type And Treatment	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range ($\mu g/L$)
F-300 Virgin[a,c] Freeze-Dried							
Chloroform	6.8	7.30	189	176-203	0.632	0.615-0.649	8.9-118
Bromodichloromethane	6.7	7.30	369	360-378	0.610	0.605-0.614	8.1-310
F-300 Virgin[b,d] Non Freeze-Dried							
Chloroform	6.7	7.30	143	139-147	0.662	0.658-0.668	1.8-807
Bromodichloromethane	6.6	7.30	401	383-419	0.607	0.599-0.614	6.7-773

[a] Carbon size: 200x400 mesh

[b] Carbon size: 325x400 mesh

[c] Initial Concentration: C_o = 2 μM/L

[d] Initial Concentration: C_o = 20 μM/L

* NLLS: Non Linear Least Squares

Temperature: 20°C

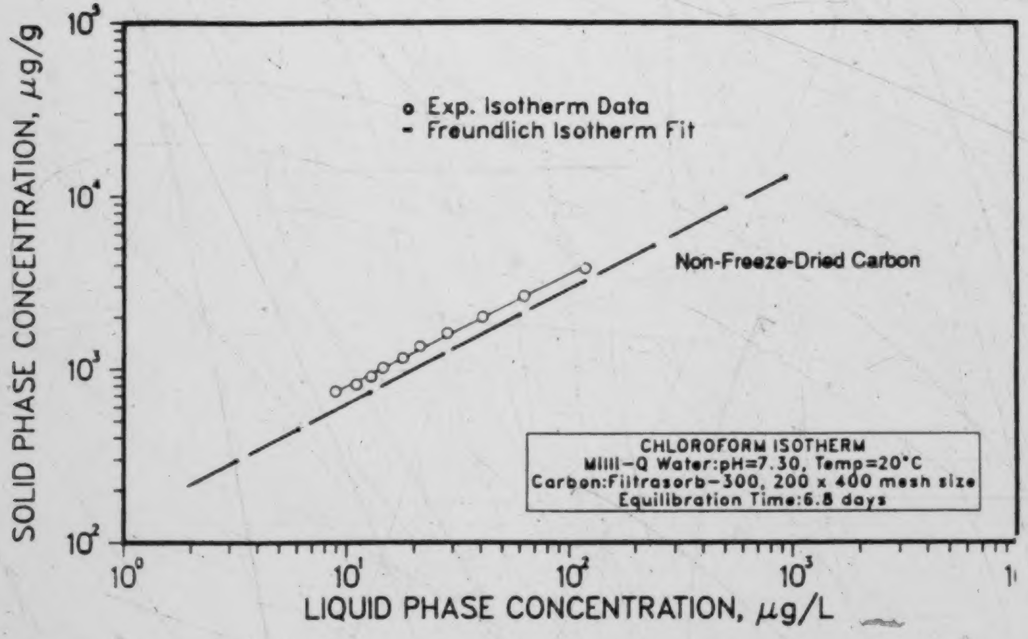


Figure 5.35 Chloroform Isotherm on Virgin Freeze-Dried F-300

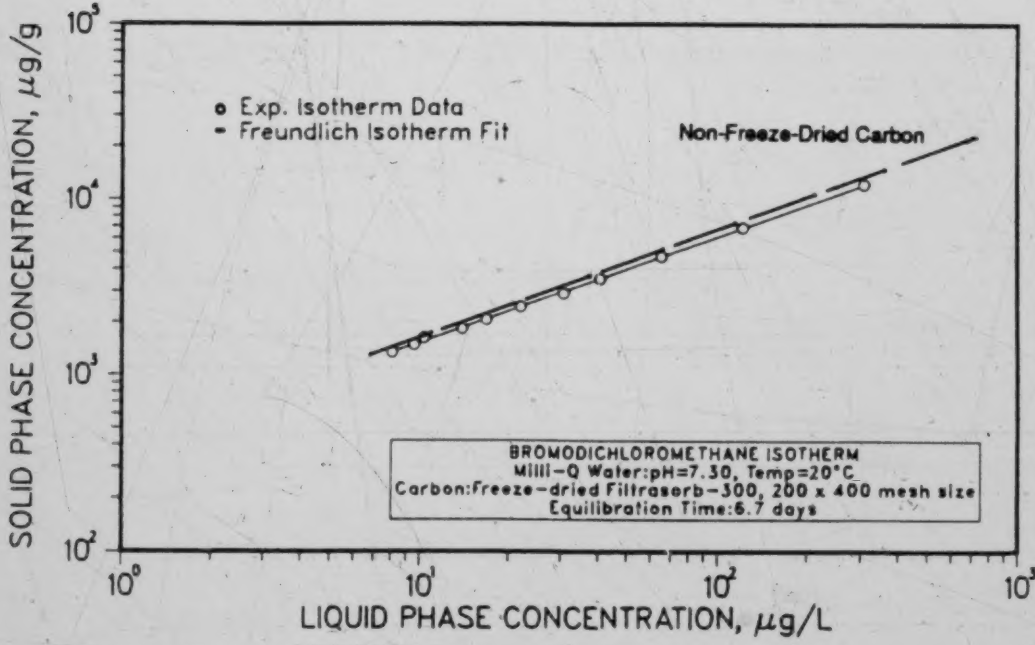


Figure 5.36 Bromodichloromethane Isotherm on Virgin Freeze-Dried F-300

Table 5.15 Apparent Density Results

Carbon Type	Apparent Density (g/mL)	Moisture Content (%)
F-300 Virgin	0.543	0.79
F-300 Virgin (Freeze-Dried)	0.537	2.36
F-300 Pre-Loaded[a] (Freeze-Dried)	0.559	2.66
Ceca 830 Virgin	0.506	2.19
Ceca 830 Virgin (Freeze-Dried)	0.511	1.92
Ceca 830 Pre-Loaded[a] (Freeze-Dried)	0.513	3.01

[a] Carbon obtained from Buffalo Pound full-scale contactors after 135 days of operation (summer 1986).

Pre-loaded carbon densities for F-300 and Ceca 830 increased by 4.1% and 0.4% respectively when compared to virgin freeze-dried carbon. Changes which occur in apparent densities can be incorporated into model input data, used to predict breakthrough.

5.6.3 Isotherm Results Using Pre-Loaded Carbon From Full-Scale Contactors

Single solute isotherms were conducted for chloroform and bromodichloromethane using freeze-dried pre-loaded Ceca 830 and F-300 carbons. Each of these carbons was a mixture obtained from full-scale GAC contactors at Buffalo Pound following a 135 day operating season (summer 1986) during which time the TTHM concentration averaged 41.1 µg/L. The F-300 carbon was obtained from the top 0.3 m of a full-scale bed whereas the Ceca 830 carbon represented a mixture of the contents of an entire bed. Since this carbon had already received considerable THM loading, these preliminary experiments were performed to estimate reduction in capacity which could be expected over an operating season at Buffalo Pound, and to serve as an aid in designing isotherm experiments. Single solute isotherm parameters which provide a comparison to F-300 virgin freeze-dried carbon are shown in Table 5.16.

A large decrease in the adsorptive capacity was evident, although some of this of course was due to pre-adsorbed THMs. The parallel shift in isotherms for trichloroethene and tetrachloroethene noted by Zimmer et al. (1987a) for pre-loading periods extending to 50 weeks was not observed. For F-300, K

Table 5.16 Isotherm Results For Freeze-Dried Carbons: (i) Virgin F-300 (ii) Pre-Loaded F-300 and (iii) Pre-loaded Ceca 830

Carbon Type	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range (µg/L)
(i) F-300 Virgin Freeze-Dried:							
Chloroform	6.8	7.30	189	176-203	0.632	0.615-0.649	8.9-118
Bromodichloromethane	6.7	7.30	369	360-378	0.610	0.605-0.614	8.1-310
(ii) F-300 Pre-loaded Freeze-Dried:							
Chloroform	6.8	7.30	20.5	15.0-25.9	0.837	0.789-0.884	40.5-418
Bromodichloromethane	6.7	7.30	121	96.1-146	0.650	0.614-0.687	20.0-423
(iii) Ceca 830 Pre-loaded Freeze-Dried:							
Chloroform	6.8	7.30	1.8	0.8-2.8	1.27	1.15-1.38	42.8-136
Bromodichloromethane	6.7	7.30	52.7	15.0-90.4	0.728	0.603-0.853	21.9-471

Carbon size: 200 x 400 mesh
Temperature: 20°C
* NLLS: Non Linear Least Squares

values represent 14% and 30% of their initial values on virgin carbon for chloroform and bromodichloromethane respectively. Pre-loaded K values for chloroform and bromodichloromethane on Ceca 830 carbon represent respectively only 2% and 15% of their initial values.

The increase in slope (1/n) shown for chloroform and bromodichloromethane suggest that a longer equilibration period was required, especially for the lower range of residual concentrations. Experimental results presented in Section 5.6.3.2 examine the effect of equilibration time for isotherms involving pre-loaded carbon. To quantitatively assess the reduction in adsorptive capacity for THMs due to gradual fouling of the carbon, a small pre-loading column was installed at the Buffalo Pound water treatment plant, as discussed previously. This column allowed 15 g samples of virgin GAC to be pre-loaded with background organics for varying lengths of time simulating startup to the end of a typical full-scale GAC operating season.

5.6.3.1 Pre-Loading Column Monitoring Results

Design and operation of a pre-loading column used to pre-load carbon with background organics for periods of 2, 4, 8, 16 and 36 weeks was described earlier in Chapter 4 (Methods). Influent and effluent samples were collected weekly, shipped to the University of Alberta, and analyzed for chloroform, bromo-dichloromethane and DOC.

For chloroform, pre-loading column influent concentrations during the pre-loading period from 3 to 14 weeks were higher than measured by Buffalo Pound personnel during the same operating time for contactor influent. In general, Buffalo Pound THM values were expected to be higher than those measured by the University of Alberta since they used direct aqueous injection (DAI) as opposed to the purge/trap method of analysis. All experimental results were checked carefully and no immediate explanation for the higher results was available except possibly the effect of sample storage at the University of Alberta prior to analyses. Therefore, the mass loadings shown for chloroform for periods exceeding three weeks must be viewed in a qualitative sense only (Table 5.17). Mass loading results are not shown for the 36 week pre-loaded carbon since this carbon represented carbon taken from a full-scale contactor which had been operated for 20 weeks during the 1986 operating season and further pre-loaded for an additional 16 weeks. This sample however was used to approximate the reduction in capacity that would exist in a full-scale contactor operated for a period greater than 20 weeks.

DOC mass loadings obtained for the pre-loading column were higher, (in some cases much higher) than those obtained in the uppermost segment of full-scale beds (Gammie, 1986). Although the pre-loading column was operated in an upflow mode, this alone should not account for the differences. Other than the possibility of biological activity, no other explanation could be found. THM capacity reductions attributable to pre-loading carbon with background organics are discussed in Section 5.6.4.

Table 5.17 Pre-Loading Column Mass Loading Data

Weeks of Pre-Loading	Cumulative Mass Loading[a] $CHCl_3$ (µg/g)	$CHCl_2Br$ (µg/g)[c]	DOC (mg/g)
2	271	135	65.4
4	167	54	88.4
8	6,730[b]	176	201
16	10,800	276	661[d]

a Cumulative mass loading results were calculated weekly, based on the amount of carbon remaining in the column and summed over the entire pre-loading period.

b The large increase in loading cannot be explained entirely by the smaller mass of carbon (60% of original total) remaining in the column.

c $CHCl_2Br$ results illustrate the loading rate expected.

d High DOC loading suggests biological activity in column.

5.6.3.2 Kinetics Results Using Pre-Loaded Carbon

A kinetics study was designed to examine the effect of equilibration time in isotherm experiments using pre-loaded carbon. A plot relating reduction in liquid phase concentration to equilibration time is shown in Figure 5.37. Following a period of one week a levelling in the decrease of reduced concentration (C/C_o) was noted. A further reduction of only 2% occured in the period between one and two weeks. Decreases after this point in time were negligible.

For all isotherm experiments involving the use of pre-loaded carbon an equilibration period of two weeks was adopted to ensure that equilibrium was attained, as closely as possible.

5.6.4 Estimation of Freundlich Parameters as a Function of Pre-Loading Time

5.6.4.1 Preliminary Investigations

Four point isotherm experiments were conducted to provide a preliminary estimate of Freundlich parameters for pre-loaded carbon. The carbons used in these experiments (F-300) had been pre-loaded for periods of 2, 4, 8, 16 and 36 weeks at the Buffalo Pound water treatment plant. Chloroform, spiked into Milli-Q® water at an initial concentration of 20 µM/L was used as the adsorbate in the isotherm experiments. The preliminary Freundlich parameters are shown in Appendix III. A plot showing the five pre-loaded isotherms with a comparison to a single solute virgin F-300 isotherm is presented as Figure 5.38. Undue emphasis should not be

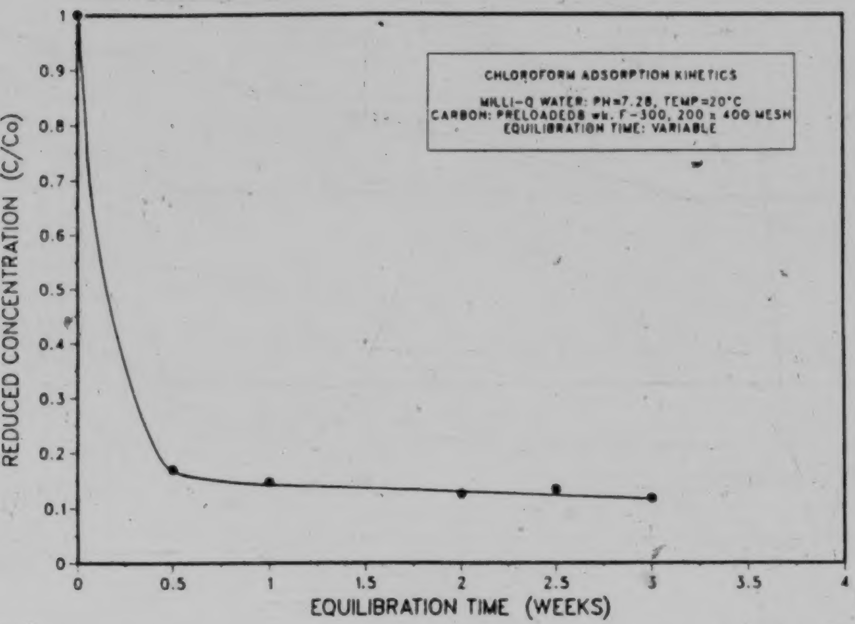


Figure 5.37 Adsorption Kinetics of Chloroform on Pre-Loaded F-300

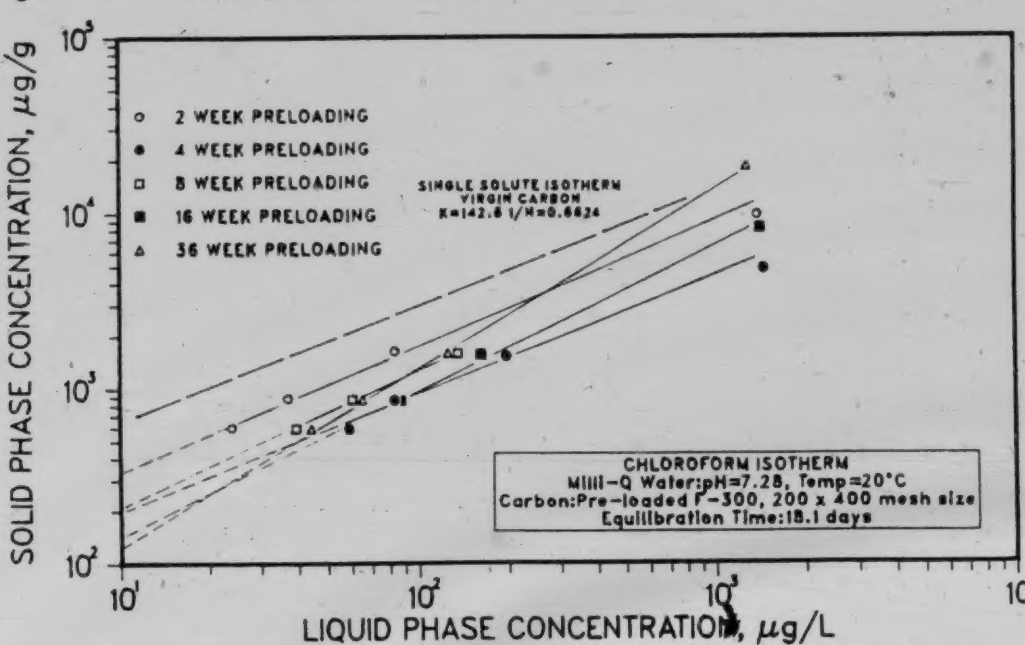


Figure 5.38 Comparison of Preliminary Chloroform Single Solute Isotherms on Virgin F-300 and F-300 Pre-Loaded for 2, 4, 8, 16 and 36 Weeks

placed on the 36 week isotherm since this carbon was initially pre-loaded under different conditions and only four data points were obtained to describe the slope. In detailed isotherm experiments described later (Figure 5.41), a lower slope was obtained for the same carbon.

As previously discussed in Section 5.3.4, K values should not be compared without also comparing 1/n values. A direct comparison among K's is appropriate only when isotherm slopes are parallel.

The results qualitatively show that a reduction in the Freundlich K parameter occurred as the pre-loading time increased. This observation was consistent with earlier findings of Zimmer et al. (1987a) for trichloroethene, 1,1,1-trichloroethane, and tetrachoroethene on Filtrasorb 100® pre-loaded with Karlsruhe tap water. Typical data from the study by Zimmer et al. (1987a) showed a downward parallel shift in isotherms following pre-loading with organics. For the Buffalo Pound data a similar parallel shift was noted for the first 8 weeks of pre-loading. Following this period an increase in the slope was observed for the 16 and 36 week pre-loaded carbon samples. In addition, these isotherms did not show a consistent decrease in capacity during the pre-loading time.

The reduction in the Freundlich K parameter due to pre-loading is shown in Figure 5.39. A large decrease was evident during the first 8 week pre-loading period. This type of decrease was consistent with findings reported by Zimmer et al. (1987a), especially for weakly adsorbing chlorinated compounds. It must be recalled that, in the present study, part of the reduction in K is due

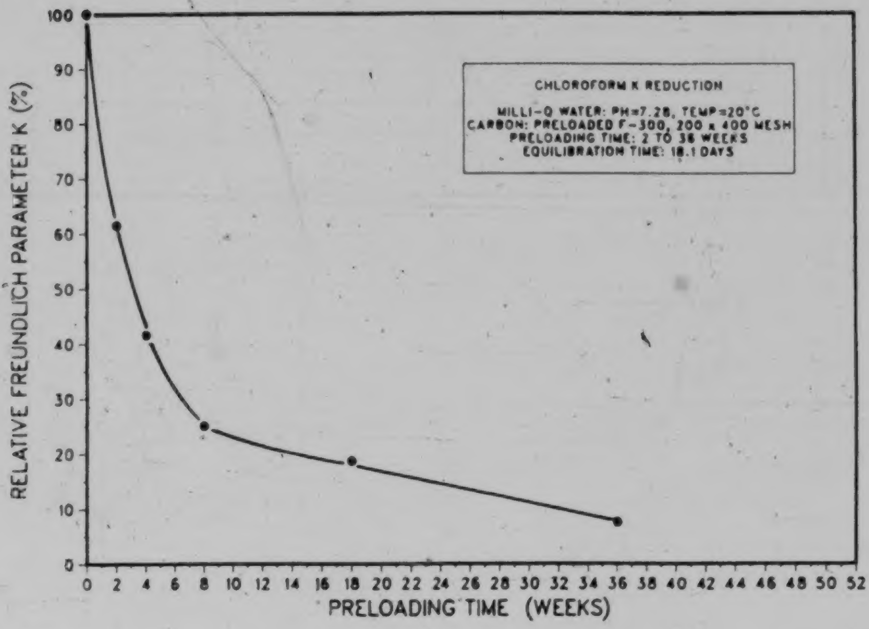


Figure 5.39 Apparent Reduction in Freundlich K for Chloroform Due to Pre-Loading With Background Organic Matter on F-300 - Preliminary Data

to the adsorption of trihalomethanes.

To determine if the reduction in adsorptive capacity (Freundlich K) could be related to the other parameters which defined the background organic loading present on the carbon, TOX analyses were conducted on individual pre-loaded carbon samples. These results are shown in Figure 5.40. Using the same time scale, when the reduction in K plot was compared to TOX accumulated, an inverse relationship was observed. Therefore, for a given compound such as chloroform it may be possible to relate residual adsorptive capacity to pre-adsorbed TOX. To confirm a hypothesis of this type however would require further study using other compounds of varying adsorptive strengths.

5.6.4.2 Evaluation of Freundlich Parameters for Chloroform on Pre-Loaded Filtrasorb 300®

On the basis of preliminary isotherm parameters, routine (12 bottle) isotherm experiments were designed and conducted to obtain precise parameter estimates over a wide concentration range. As before, the carbon used in these experiments (F-300) had been pre-loaded for periods of 2, 4, 8, 16 and 36 weeks at the Buffalo Pound water treatment plant using pre-GAC water. Results for individual Freundlich parameters from this experiment are presented in Table 5.18. Figure 5.41 shows the five isotherms on a single graph and provides a quantitative comparison to the single solute virgin F-300 isotherm. Four of the pre-loaded isotherms intersected in the liquid phase concentration range of approximately 30 µg/L to 100 µg/L. Typically, for comparison purposes Freundlich K values are evaluated

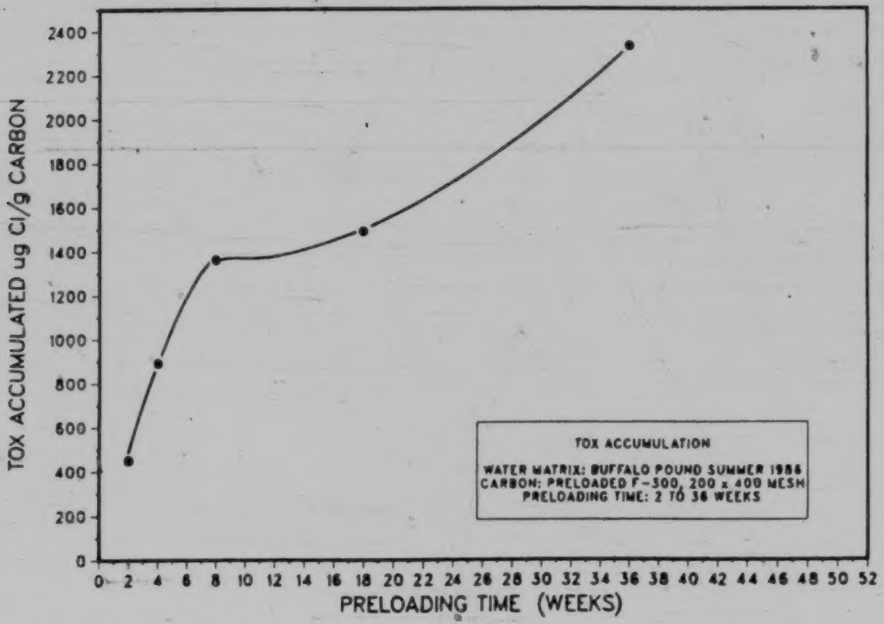


Figure 5.40 TOX Accumulation Due to Pre-Loading With Background Organic Matter on F-300

Table 5.18 Freundlich Parameters for Chloroform Adsorption on Pre-Loaded Filtrasorb 300®

Preloading Time (Weeks)	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range (µg/L)
0^a (Virgin Carbon)	6.7	7.30	143	139-147	0.662	0.658-0.668	1.8-807
2^b	13.8	7.29	43.8	22.6-65.1	0.747	0.675-0.818	28.1-1100
4^b	13.8	7.29	54.3	36.8-78.9	0.593	0.544-0.641	48.2-1200
8^b	13.8	7.29	24.1	7.73-40.4	0.783	0.690-0.876	29.7-1770
16^b	13.8	7.29	38.4	20.2-56.6	0.664	0.595-0.733	34.0-1350
36^b	13.8	7.29	22.0	-0.24-44.2	0.778	0.639-0.916	33.2-1610

[a] Carbon size: 325 x 400 mesh
[b] Carbon size: 200 x 400 mesh
* NLLS: Non Linear Least Squares

Equilibration Temp: 20°C
C_o = 20 µM/L

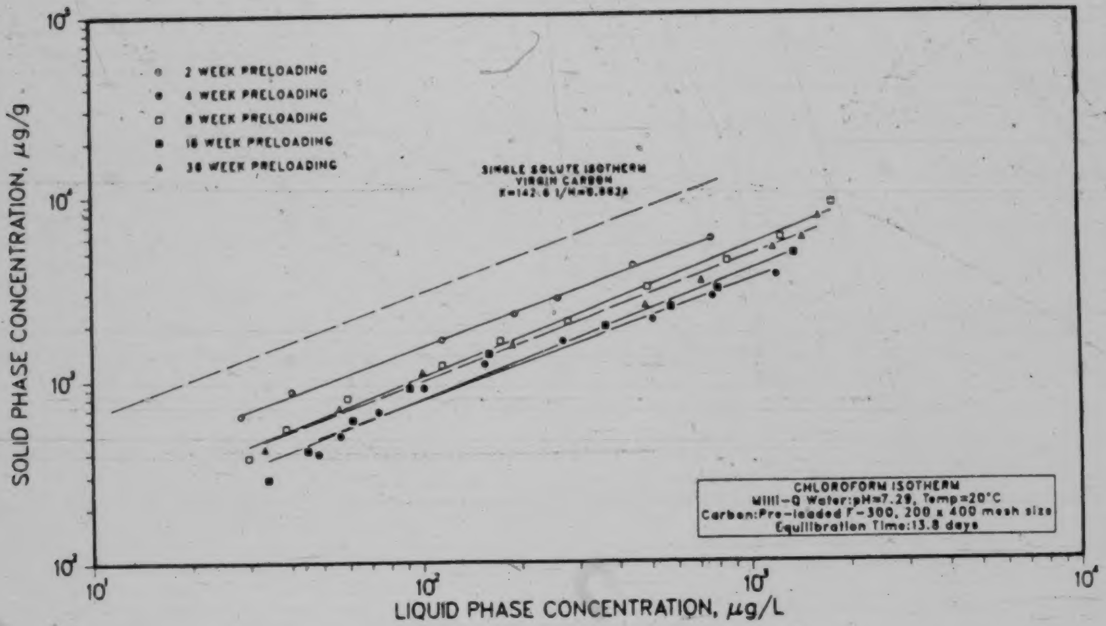


Figure 5.41 Comparison of Chloroform Single Solute Isotherms Using Virgin F-300 and F-300 Pre-Loaded for 2, 4, 8, 16 and 36 Weeks

at a residual liquid phase concentration, C_e of 1.0. Therefore, when comparing relative adsorptive capacities of the pre-loaded carbons care must be taken in selecting a suitable C_e.

As previously discussed, THM's which were unavoidably present during pre-loading may themselves have caused a partial reduction in adsorptive capacity. To evaluate the maximum possible range of effects that previously adsorbed THM's may have on the pre-loaded isotherms, a mathematical approach was applied.

The isotherm for 2 week pre-loaded chloroform was selected to serve as an example in calculations since chloroform was known to be the most weakly adsorbing THM component. The 2 week isotherm, representing the shortest period of pre-loading, would therefore be subject to the largest effects of capacity reduction due to pre-adsorbed chloroform present in the background matrix. For pre-loading periods longer than 2 weeks it is likely that chloroform would have been displaced from the carbon by more strongly adsorbing organics. Also, for pre-loading periods beyond 2 weeks, pore blockage by larger molecules would reduce the adsorption sites available to chloroform.

To represent the maximum amount of chloroform that could have been adsorbed during the pre-loading operation, an equilibrium loading value of 703 µg/g was obtained for a liquid phase concentration of 35.5 µg/L, from a chloroform isotherm previously conducted in Buffalo Pound pre-GAC water using Filtrasorb 300® carbon. The equilibrium concentration value of 35.5 µg/L obtained from Buffalo Pound operating data represents the average influent concentration for the pre-loading period of 0-2 weeks. Based on influent and effluent monitoring, the carbon in the pre-loading column was assumed to be exhausted for chloroform within the first one to two weeks of operation.

The loading value of 703 µg/g represents the maximum capacity loss for chloroform. When this value is added to the loading capacities of each isotherm point in the original 2 week pre-loaded isotherm, a new set of points is obtained as shown in Figure 5.42. The displacement from the original 2 week pre-loaded isotherm represents an approximation to the maximum capacity loss due to pre-adsorption of chloroform.

This calculated effect may be assumed to represent the maximum decrease in chloroform capacity, since the additional equilibrium capacity value of 703 µg/g was obtained from an isotherm experiment which accounted only for competition due to the co-adsorption of other background organics and not the fact that the pre-loading column carbon capacity for chloroform was also reduced by the continued exposure to adsorption of organic matter. The revised data suggest that for high carbon dosages (low liquid phase concentrations) the effect of pre-loaded chloroform is significant but as dosages decrease, the overall effect decreases, becoming negligible at low carbon dosages (high liquid phase concentrations).

To represent the capacity reduction due to pre-adsorbed chloroform in a manner more representative of actual conditions, a chloroform loading value of 271 µg/g, obtained from mass balance results for the first two weeks of pre-loading column operation was also utilized for comparative purposes in calculations. Recalculated

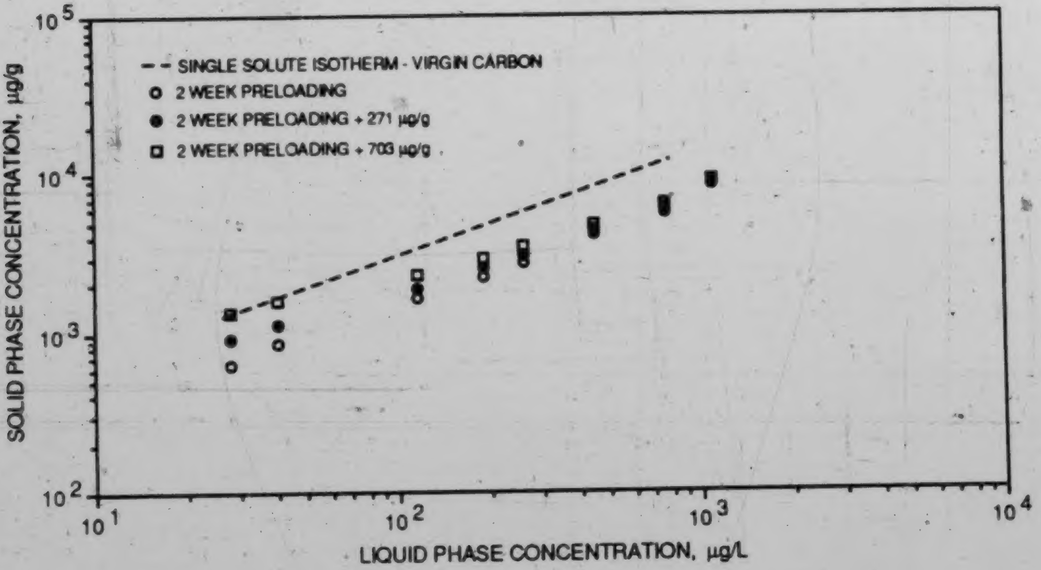


Figure 5.42 Calculated Effects of Pre-Adsorbed Chloroform on Adsorption Capacity

data using this value are shown in Figure 5.42. The impact of pre-adsorbed chloroform on the pre-loaded isotherm capacity is now much smaller than that which was based on the co-adsorption isotherm results discussed earlier. As before, the effect on capacity reduction decreases as carbon dosage increases.

It must be emphasized that the effects of pre-adsorbed chloroform on pre-loaded isotherm capacity shown in Figure 5.42 represent the worst possible case. It is expected that this capacity reduction effect of chloroform would decrease with respect to pre-loading time due to displacement of chloroform by other more strongly adsorbed background organic compounds.

Reported Freundlich parameters for pre-loaded carbon were expected to be influenced to a lesser extent due to the pre-adsorption of THM's, for chloroform pre-loading periods greater than two weeks. It may also be assumed that isotherms involving pre-loaded carbon for bromodichloromethane which was present in only very small concentrations (≤ 10 µg/L) would also be effected to a similar or lower extent. However, since the reduction in capacity attributable to pre-adsorbed THM's could not be quantified, subsequent modelling which was performed ignoring this effect may somewhat underestimate breakthrough occurrance when considering low THM concentrations.

5.6.4.3 Evaluation of Freundlich Parameters for Bromodichloromethane on Pre-Loaded Filtrasorb 300®

Following completion of the pre-loaded chloroform isotherm experiments similar experiments were designed to evaluate bromodichloromethane. Results for individual Freundlich parameters are shown in Table 5.19. A plot showing results for the five pre-loading times on one graph is presented as Figure 5.43. For pre-loading periods of 2, 8, and 16 weeks a downward shift in the isotherm lines, parallel to the pure water isotherm was observed. This behaviour was consistent with earlier pre-loading results reported for chloroform. Results for the 4 and 36 week pre-loadings did not follow the trend expected. The apparent shift in the 4 week pre-loaded isotherm cannot be easily explained. As noted earlier in the analysis of chloroform data, the slopes of the 4 and 36 week pre-loadings are respectively lower and higher than the other three pre-loading periods which appear approximately parallel. This phenomenon may be related to fluctuations in influent concentrations to the pre-loading column causing both adsorption and desorption to occur during pre-loading.

The equilibrium adsorptive capacities for the pre-loaded carbons were not statistically different except for the 2 week pre-loaded carbon which exhibited a distinct K parameter and a 1/n parameter with a narrow, only slightly overlapping confidence band (Table 5.19).

5.6.4.4 Alternate Methods to Evaluate the Effect of Pre-Adsorbed THM's on Pre-Loaded Isotherm Capacity

To evaluate the effect of pre-adsorbed THM's on pre-loaded isotherm capacity, the adsorptive capacity of two carbon samples obtained from a pilot study designed to investigate the use of various disinfectants were compared (Huck, 1988). The two carbon

Table 5.19 Freundlich Parameters for Bromodichloromethane Adsorption on Pre-Loaded Filtrasorb 300®

Preloading Time (Weeks)	Equilibration Time (Days)	pH	K $(\mu g/g)(L/\mu g)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval	Concentration Range (µg/L)
0^a (Virgin Carbon)	6.6	7.30	401	383-419	0.607	0.599-0.614	6.7-773
2^b	13.8	7.32	266	191-342	0.516	0.476-0.555	12.1-203
4^b	13.8	7.32	124	85.3-163	0.502	0.459-0.544	43.8-2210
8^b	13.8	7.32	121	86.7-155	0.582	0.543-0.621	13.5-1980
16^b	13.8	7.32	108	82.4-134	0.552	0.519-0.585	23.0-1910
36^b	13.9	7.30	111	93.7-129	0.627	0.602-0.652	5.0-667

[a] Carbon size: 325 x 400 mesh
[b] Carbon size: 200 x 400 mesh
* NLLS: Non Linear Least Squares

Equilibration Temp: 20°C
C_o = 20 µM/L

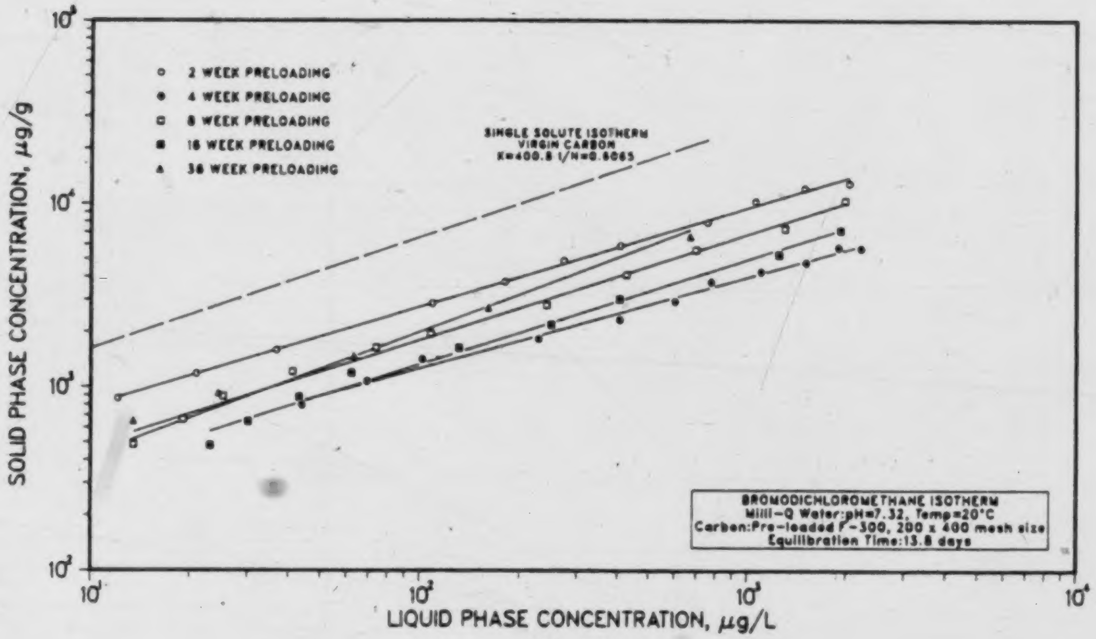


Figure 5.43 Comparison of Bromodichloromethane Single Solute Isotherms Using Virgin F-300 and F-300 Pre-Loaded for 2, 4, 8, 16 and 36 Weeks

samples were obtained from GAC pre-loading columns receiving finished water from two parallel streams of the pilot plant. One stream (chlorine stream) received chlorine prior to GAC treatment, similar to conditions at Buffalo Pound. The other stream (reference stream) did not receive any disinfection prior to entering the GAC pre-loading column. A comparison of isotherm results for chloroform using carbon from the two streams (chlorine and reference) would serve to illustrate the possible impact of chlorinated organics on overall capacity reduction due to pre-loading with background organics. The carbon used in the pilot plant was Filtrasorb 400®. Samples used in isotherm investigatons were pre-loaded for a period of approximately 4 weeks. This pre-loading time was selected since previous results obtained for Buffalo Pound showed that the largest effect of pre-loading for chloroform and bromodichloromethane occurred during the first 4 weeks (Figure 5.39).

Typical influent characteristics for the two pre-loading columns receiving water from the chlorine and reference streams are shown in Table 5.20. Chloroform isotherm results for carbon obtained from the two streams are presented in Table 5.21.

No statistical difference was observed for Freundlich parameters when the two streams were compared. Therefore it may be concluded that the presence of pre-adsorbed THM's in this water matrix did not affect the capacity reduction attributable to background organics.

A complete discussion concerning carbon obtained from the two streams, including a comparison of methods used to prepare

Table 5.20 Average Influent Characteristics for Chlorine and Reference Stream Pre-Loading Columns

Parameter	Reference Stream	Chlorine Stream
Flowrate	0.145 L/min	0.145 L/min
Free Chlorine Residual	(not chlorinated)	0.26 mg/L
Total Trihalomethanes	< 0.2 μg/L	10.7 μg/L
Non-Volatile Organic Carbon	1.7 mg/L	1.7 mg/L

Table 5.21 Chloroform Isotherm Results for Chlorine and Reference Stream Pre-Loaded Carbon

	K $(\mu M/g)(L/\mu M)^{1/n}$ NLLS Fit*	95% Confidence Interval	$1/n$ NLLS Fit*	95% Confidence Interval	Concentration Range (μg/L)
Reference Stream	32.5	2.2-62.8	0.768	0.643-0.894	13.0-1877
Chlorine Stream	39.3	1.2-77.4	0.749	0.619-0.880	20.4-1906

*NLLS: Non-Linear Least Squares

pre-loaded carbon for use in isotherms, is included in Appendix VI.

In an attempt to quantify THM's adsorbed on pre-loaded carbon, development of a method was undertaken which allowed THM's to be thermally desorbed from carbon samples prior to GC analysis. Unfortunately, because of time constraints, this method could not be brought to fruition during the course of this study. It did, however, provide valuable insight regarding the type of method which should be used to prepare pre-loaded carbon for isotherm experiments. A complete discussion of the developmental steps towards a method by which THM's may be quantified using thermal desorption is presented in Appendix VII.

5.7 Full-Scale Results

5.7.1 Typical Raw and Treated Water Quality

Buffalo Pound lake is the source of all of the potable water for Moose Jaw, Saskatchewan, and provides most of the supply for Regina. This shallow lake (mean depth 3 m) is highly eutrophic and typically experiences severe blue-green algae blooms during the summer months. The lake itself as described by Gammie and Giesbrecht (1987) is a long narrow artificial reservoir approximately 30 km long and 1 km wide. As part of the Qu'Appelle lake system the water level of Buffalo Pound Lake is maintained by controlled releases from Lake Diefenbaker located 60 km upstream on the South Saskatchewan River. Extensive algae blooms comprised mainly of *Anabaena*, *Microcystis* and *Aphanizomenon* may be attributed to high nutrient levels caused by surface run-off from farmland in combination with very warm summer lake temperatures (19-24°C). In addition to causing taste and odour problems the algae also contribute to high summer TOC levels (4-8 mg/L), increased chlorine demand (3-12 mg/L) and appreciable total trihalomethane (TTHM) formation (80-150 µg/L).

Typical raw and treated water quality parameters as represented by 1986 data are shown in Tables 5.22 and 5.23, respectively for the months of full-scale GAC operation. Complete data is included in Appendix VIII.

5.7.2 GAC Contactor Results - 1986

During the 1986 GAC operating season regenerated Ceca 830 carbon was used in six of the eight full-scale contactors. The remaining two contactors contained virgin Ceca 830 carbon and regenerated Filtrasorb 300® carbon respectively. The contactor equipped with sampling ports (contactor number 3) spaced at 0.3 m intervals was initially filled with 3 m of regenerated Ceca 830 carbon. At day 59 of the operating period an additional 56 cm of carbon, representing approximately 20% of the full bed depth was added to the top of this contactor only. This addition served as an experiment to assess whether breakthrough of taste and odour could be reduced by a partial bed addition.

Total trihalomethane breakthrough data for four selected beds are shown in Figure 5.44. In general, levels of TTHM's displayed a decreasing trend during the five month operating season. Influent levels averaged 41.4 µg/L peaking at 59 µg/L during the month of August and decreasing to 32 µg/L by the end of the operating season

Table 5.22 Raw Water Quality Data - 1986

Parameters	Units	June	July	Monthly Average Aug	Sept	Oct	Nov
PHYSICAL							
Colour (Apparent)	Pt/Co	16	14	21	20	13	9
Odour	T.O.N.	14	16	40	28	26	22
pH	pH units	8.2	8.3	8.5	7.8	7.9	8.0
Temperature	°C	18.0	19.0	19.0	13.0	8.6	2.0
Turbidity	NTU	2.4	2.1	6.1	2.8	2.2	2.1
TRACE CONSTITUENTS							
Chlorophyll a	µg/L	5	6	40	19	15	9
Nitrate/Nitrite	mg/L N	0.02	0.02	0.16	0.37	0.37	0.41
Org N (Kjeldahl)	mg/L N	0.41	0.41	0.65	0.53	0.53	0.44
Org Carbon (diss)	mg/L C	5.0	5.3	5.2	4.6	4.4	4.3
Org Carbon (total)	mg/L C	6.3	6.1	-	-	-	-
Trihalomethanes	µg/L	3	<1	1	1	1	1
CHEMICAL DOSES							
Alum	mg/L	60	60	67	56	50	50
Pre-Chlorine	mg/L	3.3	2.6	3.7	3.1	2.9	3.5
Post-Chlorine	mg/L	0.5	1.1	1.3	1.3	1.2	0.2
Free Chlorine Residual ex plant	mg/L	1.0	.9	1.0	1.0	0.9	0.9

(Adapted from Buffalo Pound Operating Data, 1986)

Table 5.23 Treated (Post-GAC) Water Quality Data - 1986

Parameters	Units	Monthly Average June	July	Aug	Sept	Oct	Nov
PHYSICAL							
Colour (Apparent)	Pt/Co	<5	<5	<5	<5	<5	<5
Odour	T.O.N.	4	4	6	6	4	7
pH	pH units	7.3	7.2	7.2	7.3	7.3	7.2
Temperature	°C	-	-	-	-	-	-
Turbidity	NTU	.07	.09	.11	.13	.10	.13
TRACE CONSTITUENTS							
Chlorophyll a	µg/L	<1	<1	-	-	-	-
Org N (Kjeldahl)	mg/L N	.24	.20	.26	.18	.19	.26
Org Carbon (diss)	mg/L C	1.9	.7	1.1	1.2	1.5	2.4
Org Carbon (total)	mg/L C	-	-	-	-	-	-
Trihalomethanes	µg/L	41	7	22	23	23	34

(Adapted from Buffalo Pound Operating Data, 1986)

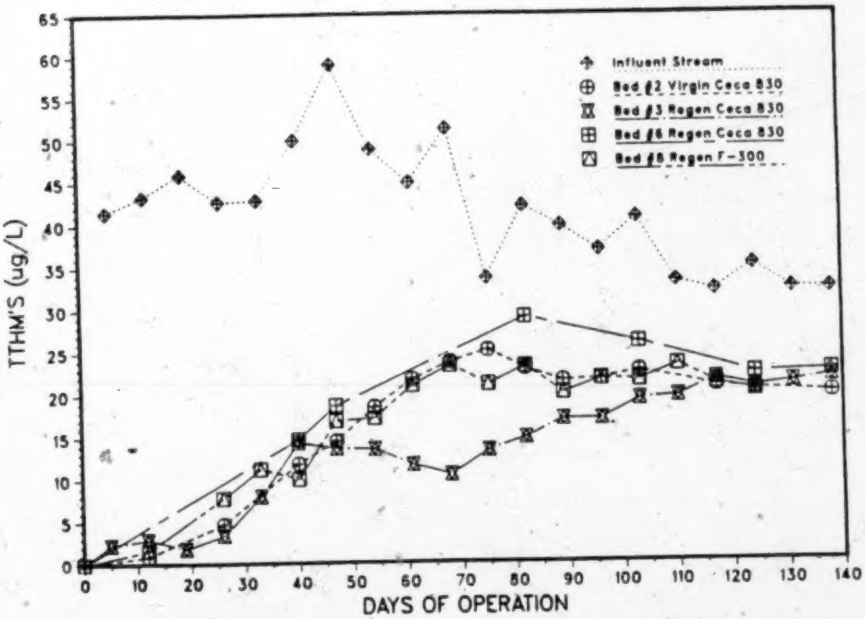


Figure 5.44 TTHM Breakthrough for Four GAC Beds During 1986 Operating Season (Adapted from Buffalo Pound Operating Data, 1986)

in November. All contactors behaved similarly with respect to removal efficiency. The decrease in effluent concentration of contactor number 3 following day 59 was directly attributable to the addition of carbon as described earlier. The effect of this carbon addition on empty bed contact time (EBCT) based on a weekly average, is shown in Figure 5.45. Trihalomethane (TTHM) breakthrough data for contactor number 3 shows that breakthrough as measured at the effluent occurs very rapidly following start-up (Figure 5.46). At the end of the GAC operating period 34% of the influent TTHM had been removed by the GAC.

Cumulative bed loadings presented in Figure 5.47 show that the capacity in the upper half of bed number 3 as represented by the three segments 0-1, 1-3, and 3-5 containing 0.3 m, 0.6 m and 0.6 m of carbon respectively, was much higher than the lower half of the bed. The overall TTHM loading for the 3.6 m bed reached 600 µg/g GAC at the end of 139 days of operation. A comparison of loading data for segments 5-8 and 8-10 indicated some desorption was occurring in the lower bed segments.

Breakthrough plots for chloroform and bromodichloromethane in the ported contactor (number 3) are shown in Figures 5.48 and 5.49 respectively. In general, breakthrough for chloroform was similar to that reported for TTHMs. This was as expected since chloroform represented approximately 70% of the TTHM concentration. Adsorption of bromodichloromethane was much stronger than for chloroform, especially in lower bed segments as indicated by the lack of convergence in the breakthrough profiles at the end of the operating season.

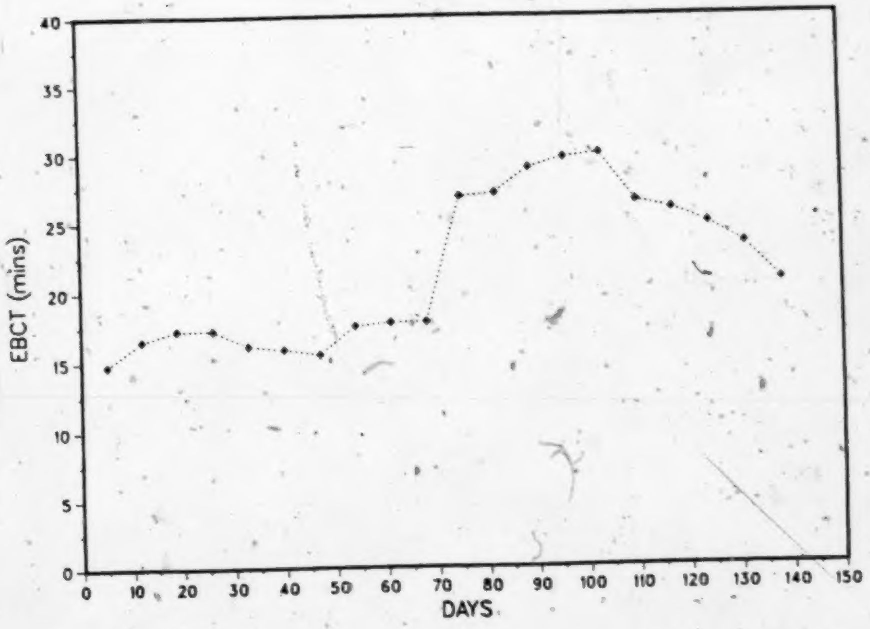


Figure 5.45 Empty Bed Contact Time for Contactor Number 3 (Ceca 830) During 1986 Operating Season (Adapted from Buffalo Pound Operating Data, 1986)

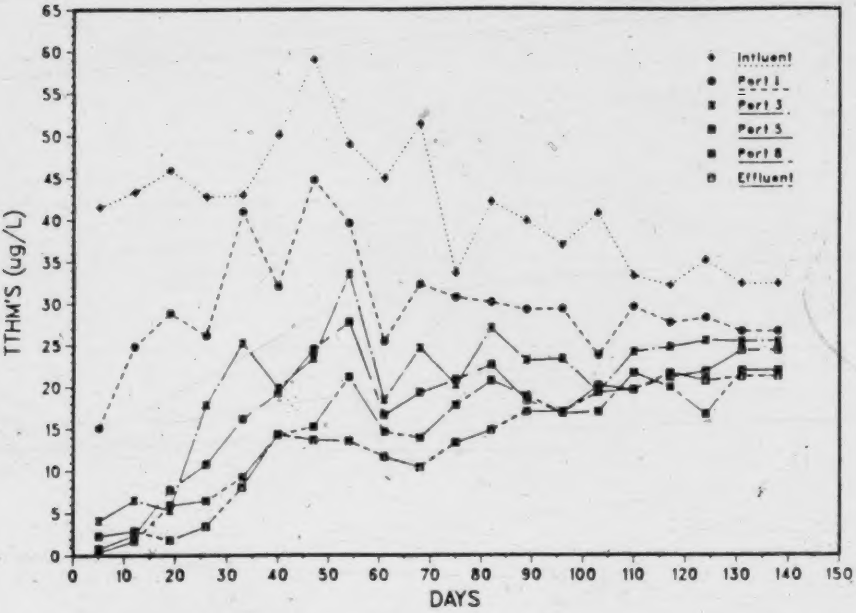


Figure 5.46 TTHM Breakthrough Profiles for Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

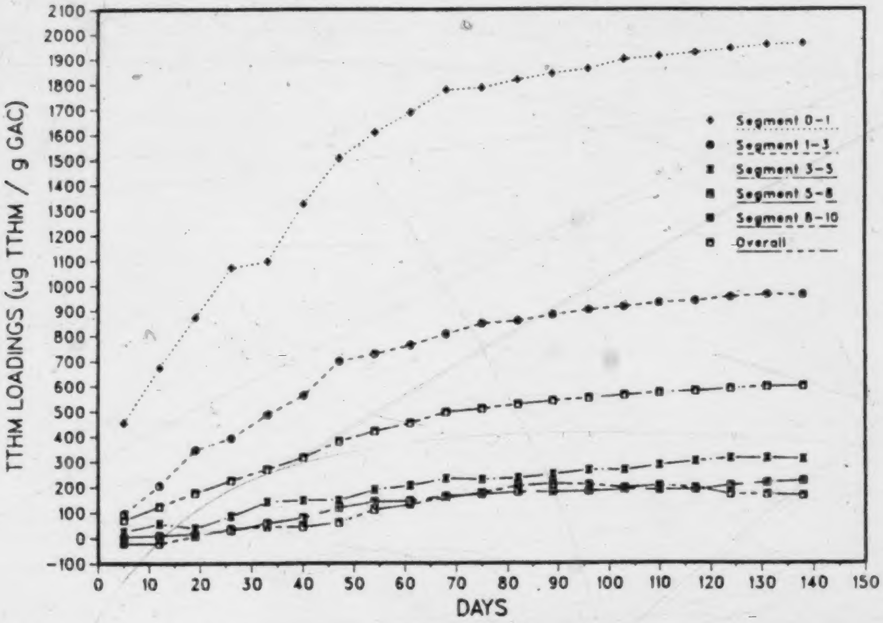


Figure 5.47 Cumulative TTHM Bed Loadings in Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

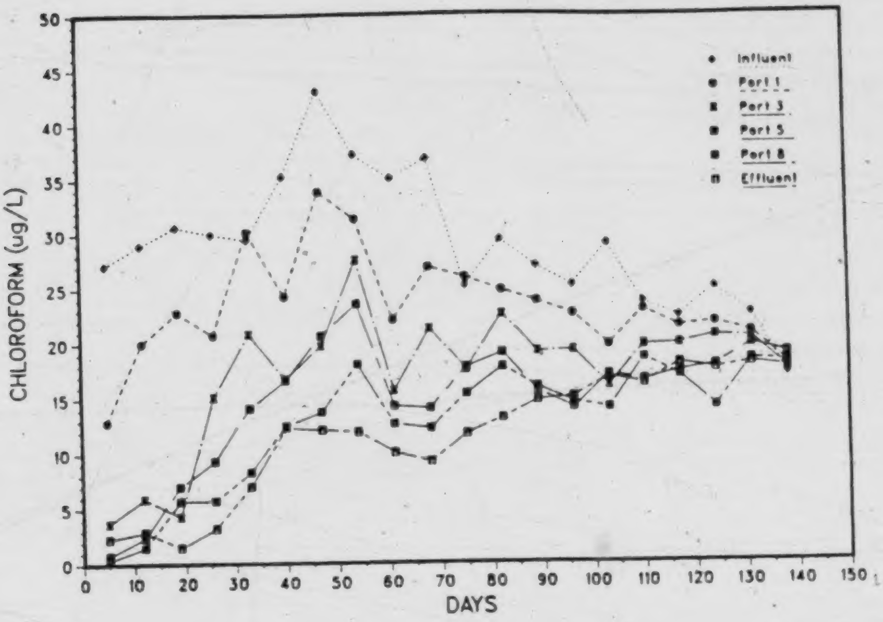


Figure 5.48 Chloroform Breakthrough Profiles for Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

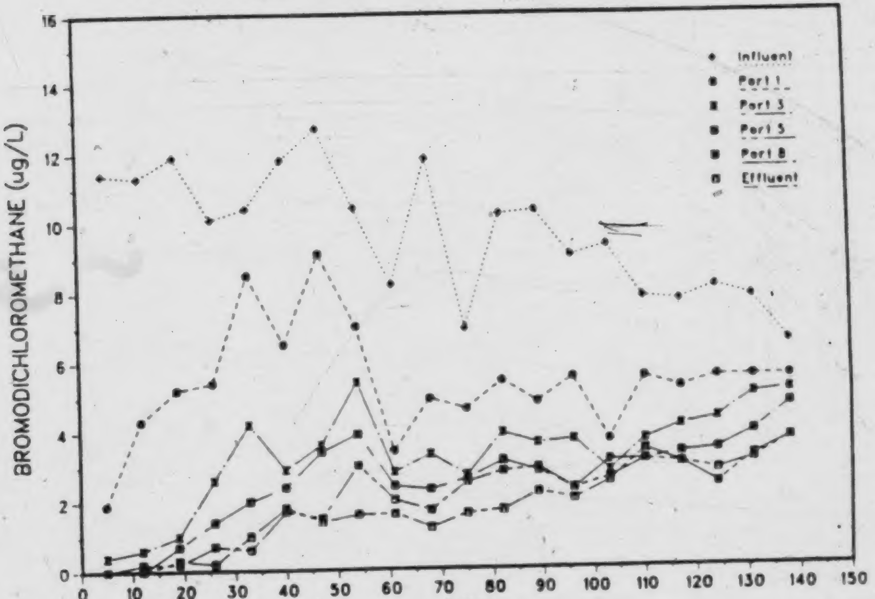


Figure 5.49 Bromodichloromethane Breakthrough Profiles for Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

Dissolved organic carbon (DOC) levels in the influent to the GAC contactors remained fairly steady during the 1986 operating season, averaging 2.7 mg/L. Breakthrough was noted immediately after start-up at all of the monitored levels in contactor number 3 (Figure 5.50). Reduction in concentration occurred at a constant rate with respect to depth except in the bottom segment as denoted by the difference in concentration between port 8 and the effluent. Following addition of 56 cm of carbon at day 59, a significant reduction in concentration was noted at all sampling ports.

DOC cumulative bed loadings are shown in Figure 5.51 for the 1986 GAC operating season. The highest loadings were obtained in segment 0-3 representing the top 0.9 m of carbon. Loadings were found to decrease with respect to depth and averaged approximately 34 mg/g GAC over the entire contactor depth following 139 days of operation. As noted earlier for TTHM's, the bottom 0.6 m of carbon (segment 8-10) displayed very poor removal efficiencies, and at times negative loadings. While this suggests that desorption was occurring during the early phase of operation (days 10-40), no immediate explanation was available. This effect is also shown later in Figure 5.58 as depicted by the crossing of wavefront lines in lower bed segments at days 19 and 40.

5.8 Equilibrium Column Model Predictions

5.8.1 Structure and Application of the Model

The equilibrium column model (ECM) allows fixed bed column breakthrough to be predicted assuming no mass transfer resistance.

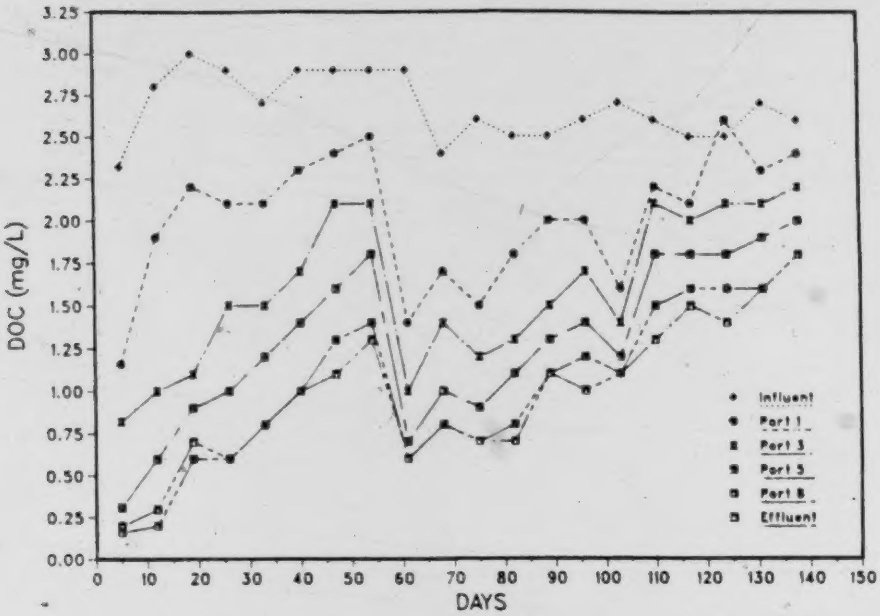


Figure 5.50 DOC Breakthrough Profiles for Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

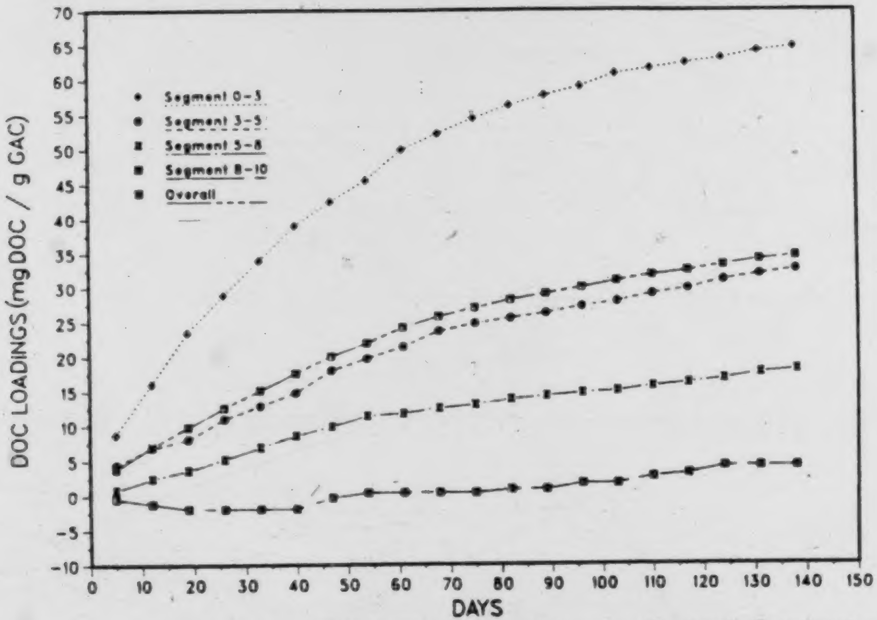


Figure 5.51 Cumulative DOC Bed Loadings in Ported Contactor Number 3 (Ceca 830) (Adapted from Buffalo Pound Operating Data, 1986)

IAST is used as a subroutine in the program to predict competition in multicomponent mixtures. Typically the program uses single solute isotherm parameters and individual component influent concentrations as input. Since the model ignores mass transfer resistance, the characteristic "S-shaped" breakthrough curve is not predicted. Instead a vertical wavefront is assumed to exist for each solute.

The ECM divides a carbon bed into zones. Each zone contains a fraction of each of the solutes, the length of which is dependent upon their relative adsorbability. The zone nearest the top of the bed contains all solutes but predominantly the most strongly adsorbing component. The second zone down the column contains the next most strongly adsorbing component. In the case of a three component mixture, the most weakly adsorbing component would be present in all three zones, but predominantly in the zone nearest the bottom of the bed. The basic equations describing column profiles for individual components are presented elsewhere by Luft (1984).

As the top portion of the bed (Zone 1) becomes saturated by the strongest adsorbing component it will cause the more weakly adsorbed components to be displaced downward at concentrations higher than present in the influent. This type of competitive displacement continues until the most weakly adsorbing component enters the bottom zone in the column at a concentration higher than in any previous zone. This is referred to as an "overshoot" concentration.

For each zone in the bed, the ECM predicts; (1) bed volumes fed to breakthrough, (2) velocity of the center of mass for each wavefront, and (3) treatment capacity (minimum carbon use rate) for individual components. The model also predicts for each component: the concentration in individual zones, the average surface loading, and the single solute treatment capacity based upon input Freundlich parameters.

5.8.2 Comparison of ECM Predictions to Full-Scale Results

ECM predictions were compared to full-scale contactor results for both the 1986 and 1987 operating periods. In 1986 comparisons were made to the Ceca 830 (ported bed) and Filtrasorb 300® carbons. In 1987 only data concerning the Filtrasorb 300® (ported bed) was evaluated since this was the only bed monitored in detail for individual THM components.

In order to examine the overall usefulness of the ECM, which ignores mass transfer resistances, Freundlich parameters used as input data included single solute isotherm results, pre-loaded carbon isotherm results, and hypothetical components (HC's), in various combinations. The methods used to obtain HC's and pre-loaded carbon capacities were discussed in Sections 5.5.2 and 5.6.4 respectively. Since no actual pre-loading involving the Ceca 830 carbon was conducted, a similar capacity reduction as obtained for Filtrasorb 300® carbon was applied. Influent concentrations for the adsorbates, chloroform and bromodichloromethane were obtained from Buffalo Pound full-scale operating data. Averaged values were used as model input. Actual variations in influent concentrations for chloroform and bromodichloromethane during the operating period are shown later in Figures 5.70 and 5.71, respectively.

5.8.2.1 Bed Capacity Predictions

Carbon usage rates, expressed as mg carbon/L water treated, predicted using the ECM were compared to estimates using single solute capacities at actual influent concentrations. The equations shown below, described by Crittenden et al. (1987b), were used by the ECM to calculate the number of bed volumes fed (BVF) to breakthrough and carbon usage for individual components.

$$BVF_i = \left(\frac{V_f}{V_{wi}} \right) \cdot \varepsilon \qquad (5\text{-}4)$$

$$\text{Usage Rate} = \left(\frac{\rho_B}{BVF_i} \right) \qquad (5\text{-}5)$$

Where:
BVF_i = bed volumes fed to breakthrough for component i
V_f = interstitial fluid velocity (m/s)
V_{wi} = velocity of wavefront for component i (m/s)
ε = bed void fraction
ρ_B = bulk density of bed (kg/m^3)

Since the ECM ignores mass transfer resistances, the predicted usage rate and BVF will be the lowest and highest possible respectively. Carbon usage rates are shown in Table 5.24 for the three full-scale beds evaluated. The single solute usage rates calculated on the basis of pure water isotherms were always slightly lower, but agreed well with ECM predictions. The cumulative single solute usage rates overestimated the amount of carbon required when compared with ECM predictions. Therefore in

Table 5.24 Comparison of ECM Capacity Predictions (Usage Rate) to Single Solute Capacity Predictions

(a) Ceca 830 - 1986

Component	Freundlich K $(\mu g/g)(L/\mu g)^{1/n}$	Freundlich 1/n	Average Influent Conc. (μg/L)	Carbon Usage Rate (mg carbon/L water)		
				Single Solute Capacity		ECM
				Individual	Cumulative	Prediction
Bromodichloromethane	354.5	0.5683	9.7	7.5	7.5	8.7
Chloroform	79.51	0.7074	28.9	33.7	41.2	34.6

(b) Filtrasorb 300 - 1986

Component	Freundlich K $(\mu g/g)(L/\mu g)^{1/n}$	Freundlich 1/n	Average Influent Conc. (μg/L)	Carbon Usage Rate (mg carbon/L water)		
				Single Solute Capacity		ECM
				Individual	Cumulative	Prediction
Bromodichloromethane	400.8	0.6065	9.7	6.1	6.1	7.9
Chloroform	142.6	0.6624	28.9	21.8	27.9	22.6

(c) Filtrasorb 300 - 1987

Component	Freundlich K $(\mu g/g)(L/\mu g)^{1/n}$	Freundlich 1/n	Average Influent Conc. (μg/L)	Carbon Usage Rate (mg carbon/L water)		
				Single Solute Capacity		ECM
				Individual	Cumulative	Prediction
Bromodichloromethane	400.8	0.6065	9.1	5.9	5.9	7.9
Chloroform	142.6	0.6624	32.0	22.6	28.5	23.3

the absence of competition with background organics or reduction in carbon capacity attributable to pre-loading, the ECM may be assumed to generate usage rates which would be similar to single solute predictions.

5.8.2.2 Comparison of Breakthrough Predictions to Full-Scale Results

Breakthrough predictions using the ECM were compared to full-scale results for two carbon beds in 1986 and one carbon bed in 1987. A typical ECM breakthrough prediction for the four trihalomethanes known to exist in Buffalo Pound finished water is shown in Figure 5.52. This figure illustrates the bed volumes at which each component would break through and the corresponding overshoot concentration. An overshoot concentration is a result of displacement by the more strongly adsorbed components. The prediction shown used the average surface loading rate and influent concentrations for the four components for the 1986 full-scale contactor operating season. The Freundlich parameters for this initial prediction represented those obtained in organic free water and neglect competition by background organics or capacity reduction attributable to pre-loading. Prior to incorporating these variables into further predictions, the desired number of components to be predicted was reduced to two, chloroform and bromodichloromethane, since these represented the major contributors to total trihalomethanes present at Buffalo Pound. Average influent concentrations for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ for the 1986 GAC operating season were 28.9, 9.6, 2.3 and <1.0

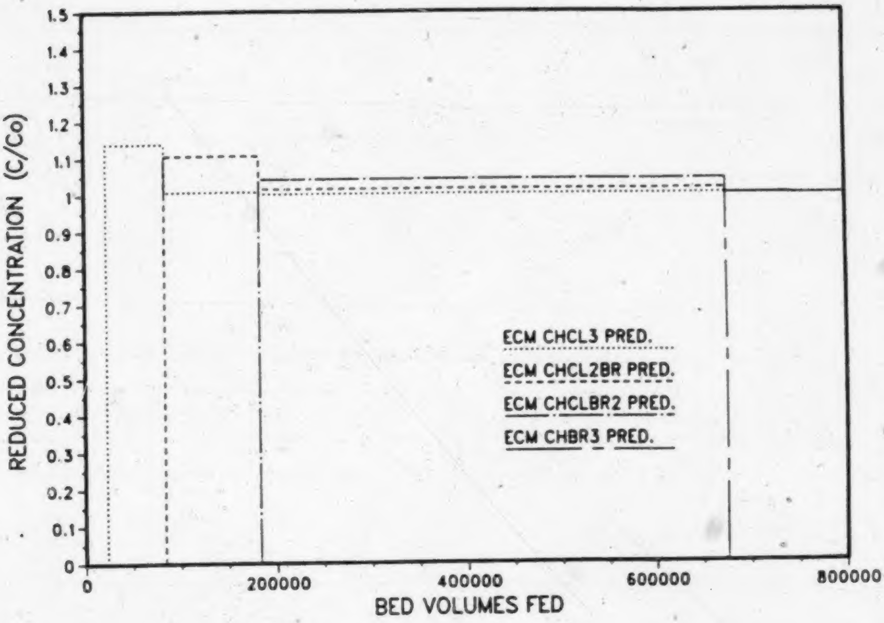


Figure 5.52 ECM Breakthrough Predictions Using Single Solute Freundlich Parameters on Ceca 830 (4 Components)

µg/L respectively. Thus $CHCl_3$ and $CHCl_2Br$ represented 92% of the total trihalomethanes. A breakthrough plot using only $CHCl_3$ and $CHCl_2Br$ as input data to the ECM is shown in Figure 5.53, using an expanded scale on the horizontal axis. In all further predictions $CHClBr_2$ and $CHBr_3$ were assumed to be a small part of the background matrix as represented by hypothetical components.

5.8.2.2.1 Ceca 830 Ported Bed - 1986 Results

Prior to the 1986 operating season, regenerated Ceca 830 carbon was placed in a full-scale contactor equipped with stainless steel ports which allowed monitoring of liquid phase concentrations at pre-selected depths. The ports themselves were spaced at approximately 30 cm (1 foot) intervals down the side of the 3.05 m (10 foot) deep contactor and extended 45 cm into the carbon. Ports designated as numbers 1, 3, 5 and 8 represented carbon depths of 30, 90, 150 and 240 cm respectively. Column effluent was monitored at port 10. The average chloroform influent concentration to the contactor was 28.9±6.1 µg/L, showing a decreasing trend during the last fifty days of operation (Figure 5.48).

Chloroform breakthrough monitored during the 1986 operating season at five different depths is shown in Figure 5.54. This data was plotted as reduced concentration, (instantaneous C/C_0) versus "whole" bed volumes fed. Fluctuations in the C/C_0 values were likely attributable to fluctuating influent concentrations. An examination of the concentration data at the end of the operating period showed that the effluent concentration exceeded the influent concentration at all monitoring locations. This "overshoot"

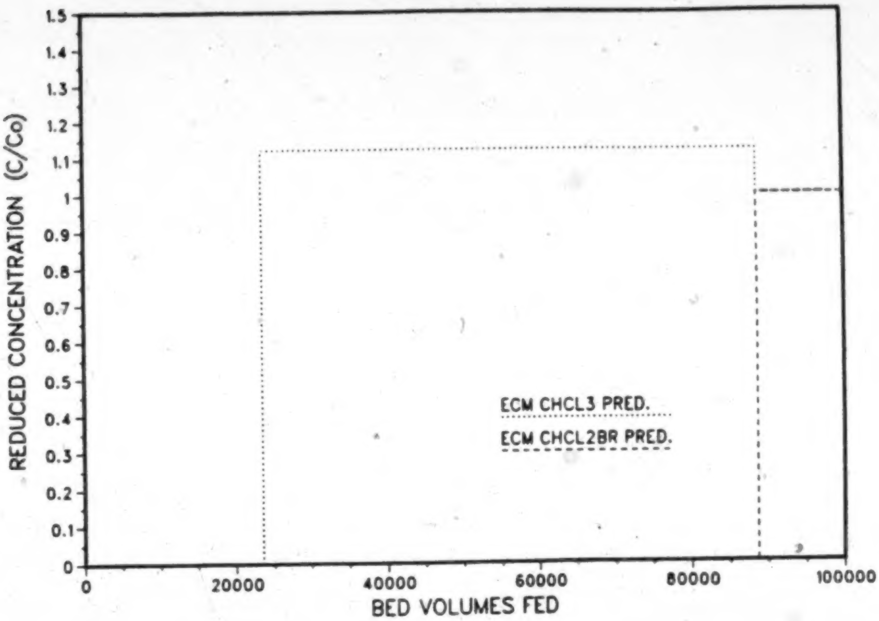


Figure 5.53 ECM Breakthrough Predictions Using Single Solute Freundlich Parameters on Ceca 830 (2 Components)

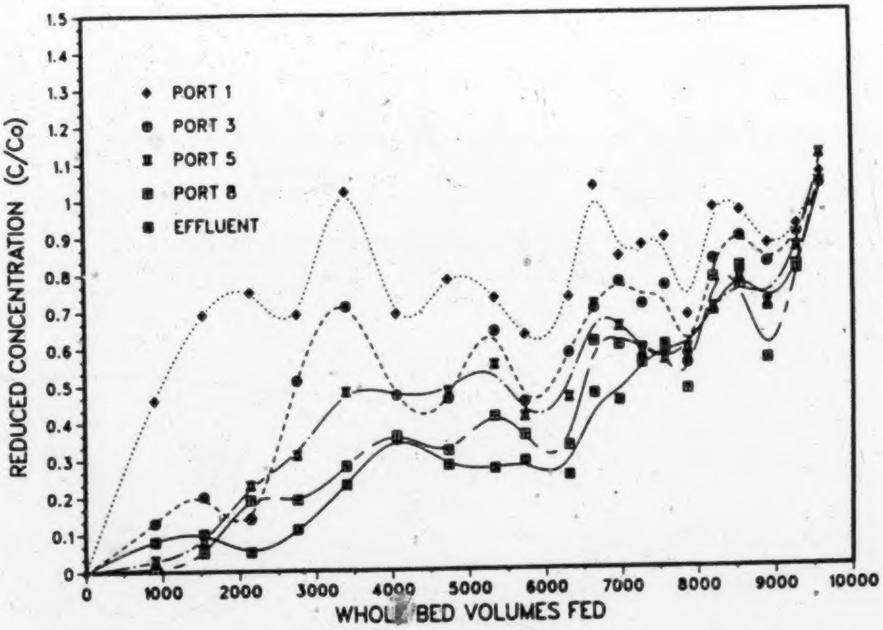


Figure 5.54 Reduced Concentration Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

concentration was either due to displacement by more strongly adsorbed chlorinated organics, or to desorption caused by a decrease in influent concentration. The term "whole" bed volumes represents a volume equivalent to the entire volume of the bed. To maximize the application of ECM predicted breakthrough data, the full-scale bed was studied in terms of five different increasing bed depths. These were now represented by the segments 0-1, 0-3, 0-5, 0-8 and 0-10 (bottom of bed). To relate these individual depths in terms of flow to the entire bed, the bed volumes fed to each segment were "normalized" such that they could be directly compared to the full bed depth. As an example, the normalized bed volumes fed to segment 0-3 could be equated to full bed volumes as shown below:

$$\begin{matrix}\text{Normalized Bed Volumes}\\ \text{(Segment 0-3)}\end{matrix} = \left(\frac{\text{Whole bed volume}}{\text{Bed volume to port 3}}\right) * \begin{matrix}\text{Whole bed}\\ \text{volumes fed}\end{matrix} \qquad (5\text{-}6)$$

As a result it was assumed that the segment 0-3 came into contact with 3.33 times the bed volumes seen by the entire bed. Chloroform breakthrough plotted versus "normalized" bed volumes is shown in Figure 5.55. This type of conversion was applied to $CHCl_3$ and $CHCl_2Br$ breakthrough data obtained for both 1986 and 1987. It allowed ECM results to be compared directly to the full-scale beds evaluated in terms of five increasing depths. The single data point shown at the end of each curve (Figure 5.55) represents the highest reduced concentration obtained for the five different depths. Breakthrough curves obtained for lower bed regions (Port 5, Port 6 and Effluent) were observed to move progressively to the left,

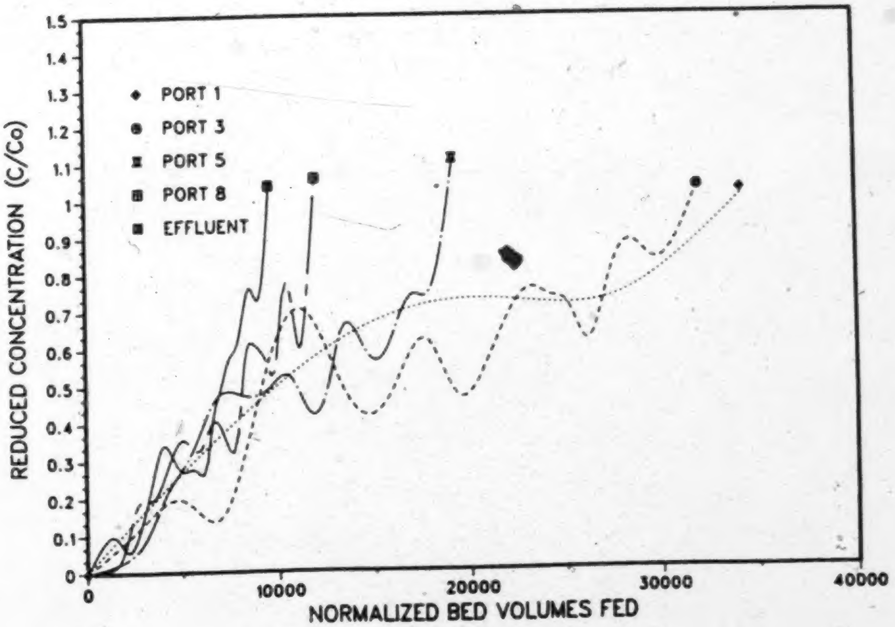


Figure 5.55 Reduced Concentration Chloroform Breakthrough (1986 Ceca 830 Ported Bed) Using Normalized Bed Volumes

suggesting that the capacity for chloroform was greatly reduced.

All ECM breakthrough predictions were conducted using the four different types of input data listed below:

Type I: Single solute isotherm parameters obtained using virgin carbon only,

Type II: Single solute isotherm parameters obtained using virgin carbon + hypothetical components (HC's) representing background competition,

Type III: Single solute isotherm parameters obtained using carbon pre-loaded for 2 weeks,

Type IV: Single solute isotherm parameters obtained using carbon pre-loaded for varying periods of time + (2,4,8,16 and 36 weeks) hypothetical components (HC's) representing background competition.

Predictions using type I data provided estimates of the maximum bed volumes fed (BVF) to breakthrough whereas predictions using type II, III or IV data provided consistently lower but more realistic estimates.

A comparison of full-scale breakthrough data to ECM estimates using type I and II input data is shown for chloroform in Figure 5.56. Since the ECM ignores mass transfer resistances, a prediction representing breakthrough in the full-scale beds (where mass transfer resistances exist) should occur at approximately midpoint ($C/C_0 = 0.5$) in the breakthrough curve. In the case of this plot for $CHCl_3$, the BVF to breakthrough were significantly overestimated for

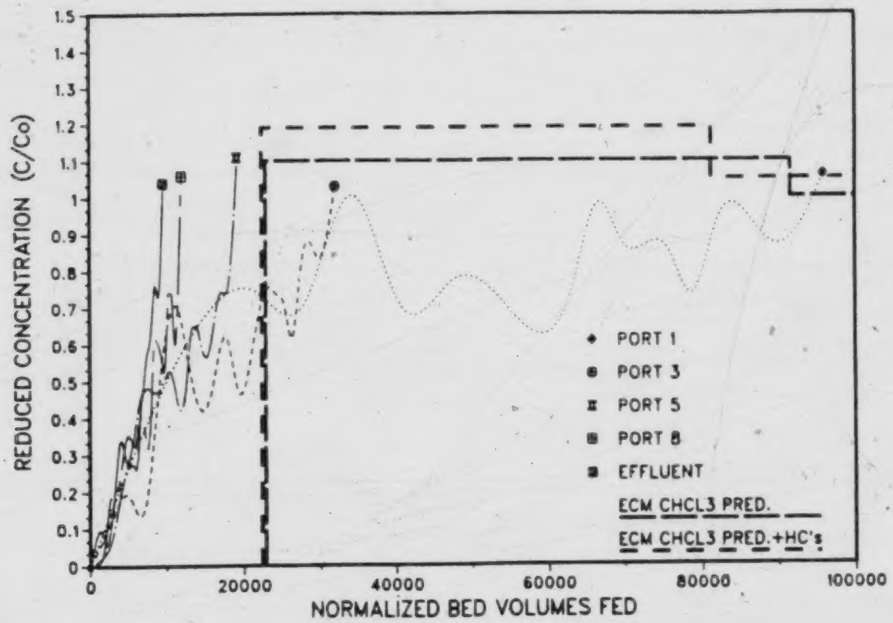


Figure 5.56 Effect of HC's on ECM Prediction of Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

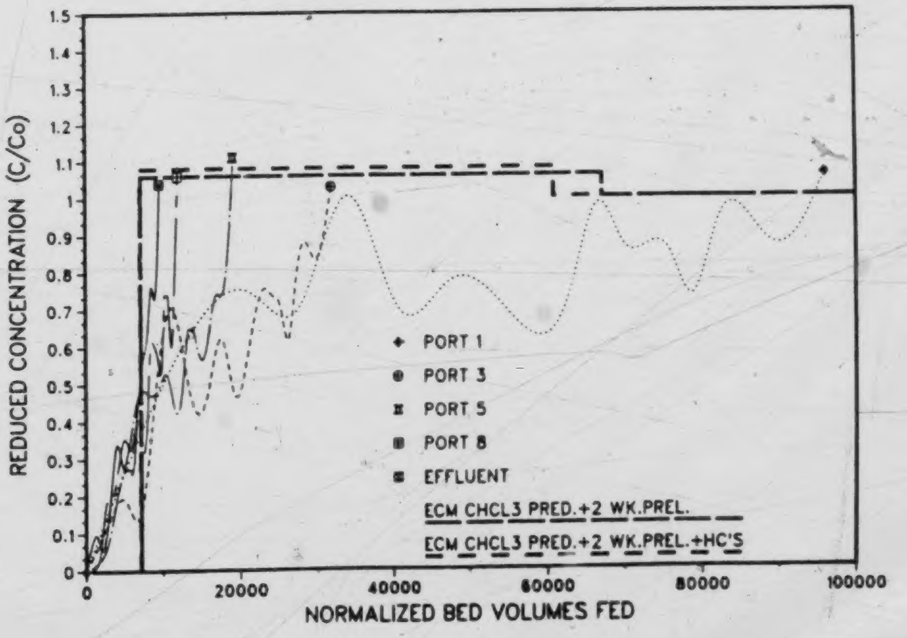


Figure 5.57 Effect of Pre-Loading and HC's on ECM Prediction of Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

the three deepest bed depths. The addition of HC's representing background competition caused a reduction in BVF by only 2%. Reduced concentration data shown for port 1 (segment 0-1) fluctuated after reaching an initial overshoot concentration at approximately 33,000 bed volumes, most likely due to variations in the influent concentration.

The effect of incorporating Freundlich parameters obtained using pre-loaded carbon alone as input data (type III data), and in combination with HC's (type IV data), is shown in Figure 5.57. A dramatic decrease in BVF was evident when pre-loading was taken into account. A negligible decrease in BVF may be attributed to HC's. Very good agreement between ECM predicted BVF to breakthrough and the midpoint in actual breakthrough curves was observed. The overshoot concentration obtained immediately prior to full-scale contactor shutdown also agreed well with ECM predictions both with and without HC's present. Since competition from other background organics was known to exist and accounts for at least some apparent capacity reduction HC's were retained in the ECM input data for predictions involving carbon pre-loaded for varying periods of time (type IV data).

To determine the appropriate length of pre-loading time that would be required for accurate ECM predictions, Freundlich parameters obtained for pre-loading times of 2, 4, 8, 16 and 36 weeks were used individually as input data. Plotted breakthrough results are shown in Appendix IX. A comparison of actual breakthrough data for a reduced concentration (C/C_0) of 0.5 to ECM predictions suggests that a pre-loading time of two to four weeks

(Table 5.25) would be appropriate for predicting BVF to breakthrough. In the full-scale bed approximately 50% breakthrough was observed to occur at mid-depth following 35 days of operation (Figure 5.48). Either a 2 or 4 week pre-loading time provides good estimates of overshoot concentrations, however the two week pre-loading period appears to provide an overshoot value which more closely approximates the effluent concentration. ECM breakthrough predictions based upon 8 to 36 week pre-loading times are shown in Table 5.25. In general, parameter estimates based on pre-loading periods in excess of 4 weeks caused BVF to breakthrough to be underestimated. This may however be useful if a reduced concentration (C/C_0) of less than 0.5 is desired to represent breakthrough as measured at the column effluent. Predicted overshoot concentrations remained consistently accurate for all pre-loading input variables. It should be recalled that the impact of pre-adsorbed THM's on carbon used to obtain Freundlich parameters, although thought to be small, may cause BVF to breakthrough values to be slightly underestimated since the residual capacity for THM's may be higher than determined experimentally.

The ECM was found to predict BVF to midpoint breakthrough that agreed well when compared to full-scale effluent results, despite the fact that wide mass transfer zones existed in the full-scale bed. Figure 5.58 shows the TTHM wavefront progression for the ported bed during the 1986 operating season. This figure may be used to illustrate chloroform breakthrough since this compound contributed approximately 70% of the TTHM. The wavefront progression shows that the front was very broad and extended over

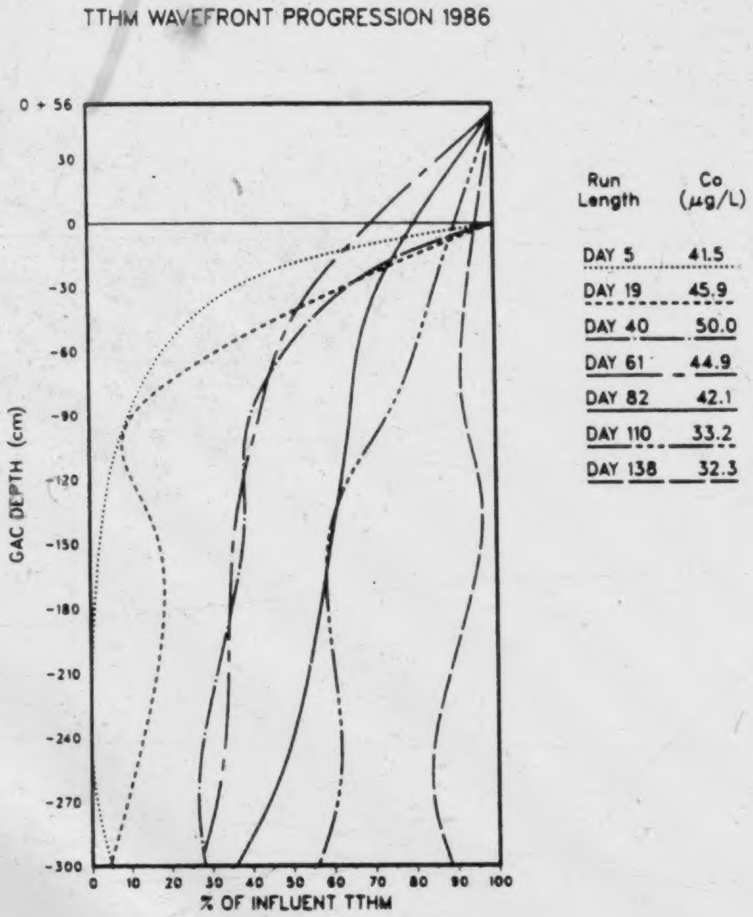
Table 5.25 Comparison of ECM Predictions to Full-Scale 1986 Chloroform Data for Ceca 830 Ported Contactor

	Normalized Bed Volumes Fed to Breakthrough								
Column Segment	Full Scale Bed (C/C_o=0.5)	ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0 - 1	10,000	23,050	22,544	7,170	7,126	8,665[a]	3,910	6,167[b]	3,571
0 - 3	9,143	23,050	22,544	7,170	7,126	8,665[a]	3,910	6,167[b]	3,571
0 - 5	9,714	23,050	22,544	7,170	7,126	8,665[a]	3,910	6,167[b]	3,571
0 - 8	8,286	23,050	22,544	7,170	7,126	8,665[a]	3,910	6,167[b]	3,571
0-Effl.	7,143	23,050	22,544	7,170	7,126	8,665[a]	3,910	6,167[b]	3,571

Actual full-scale operation time = 19.9 weeks

[a] BV fed to breakthrough exceeds value reported for previous pre-loading time due to increase in Freundlich K parameter

[b] BV fed to breakthrough value appears anomalous due to large increase in Freundlich K parameter



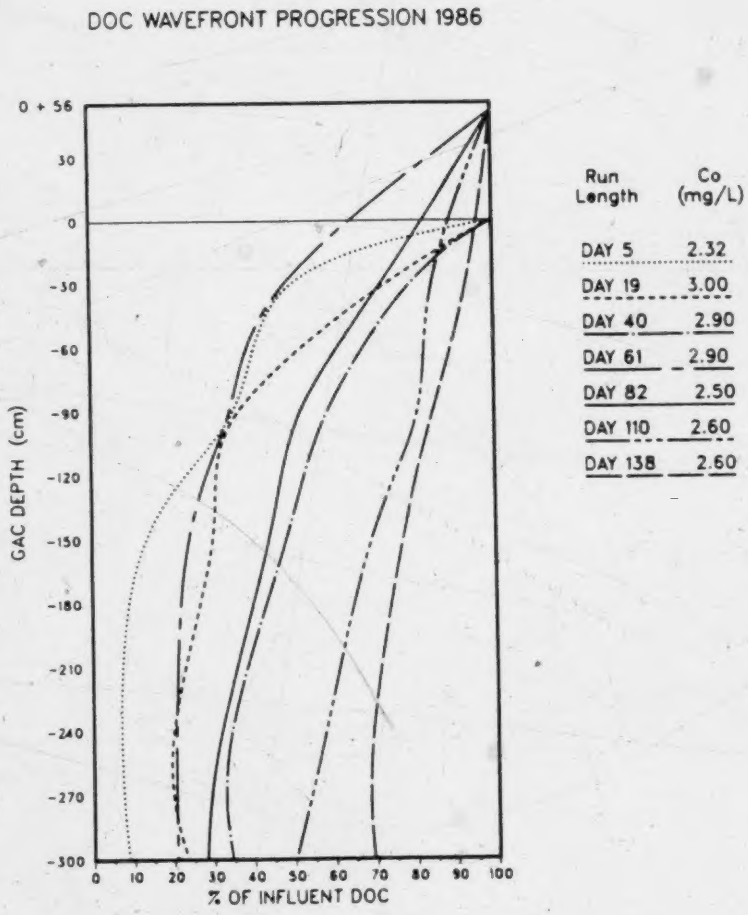
Note: 56 cm of carbon added to top of 3.05 m bed at day 59. Liquid phase samples collected at the same ports as before.

Figure 5.58 TTHM Wavefront Progression (1986 Ceca 830 Ported Bed) (Adapted from Buffalo Pound Operating Data, 1986)

the entire depth of the bed. Similar results were presented by Gammie and Giesbrecht (1986) for the 1985 operating period. Once the upper half of the bed had been exhausted very poor removals were observed in lower depths. This occurrence may be attributed at least in part to pre-loading with background organics at the lower contactor depths.

For both Figures 5.58 and 5.59 the increase in removal efficiency noted when going from day 40 to day 61 may be largely attributed to the addition of 56 cm of carbon at day 59. Routine monthly backwashing however would have reduced the longevity of this added capacity, especially in upper portions of the bed. Figure 5.59 shows the dissolved organic carbon wavefront progression. A broader wavefront than observed for TTHM's occured during the early part of the operating season. This showed that background organics which competed with THM's for adsorption sites were adsorbed to a larger extent in middle and lower bed segments, thus reducing the capacity for THM's. The positive slope noted throughout the operating period also suggests that DOC was more easily adsorbed than THM's in lower bed segments. The possible role of biological removal however must also be considered. In general, to obtain meaningful ECM predictions, pre-loading would have to be taken into account since it has been shown to influence adsorption parameters.

Bromodichloromethane breakthrough data were subjected to the same normalization procedure as discussed earlier for chloroform. Observed breakthrough data prior to and following normalization are shown in Figures 5.60 and 5.61, respectively. Complete breakthrough was not observed for this compound since it



Note: 56 cm of carbon added to top of 3.05 m bed at day 59. Liquid phase samples collected at the same ports as before.

Figure 5.59 DOC Wavefront Progression (1986 Ceca 830 Ported Bed) (Adapted from Buffalo Pound Operating Data, 1986)

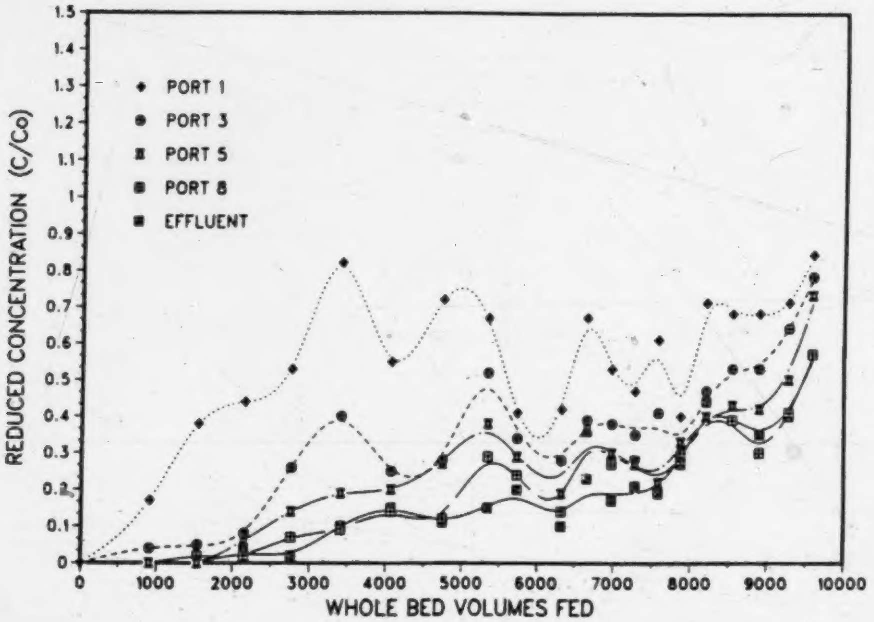


Figure 5.60 Reduced Concentration Bromodichloromethane Breakthrough (1986 Ceca 830 Ported Bed)

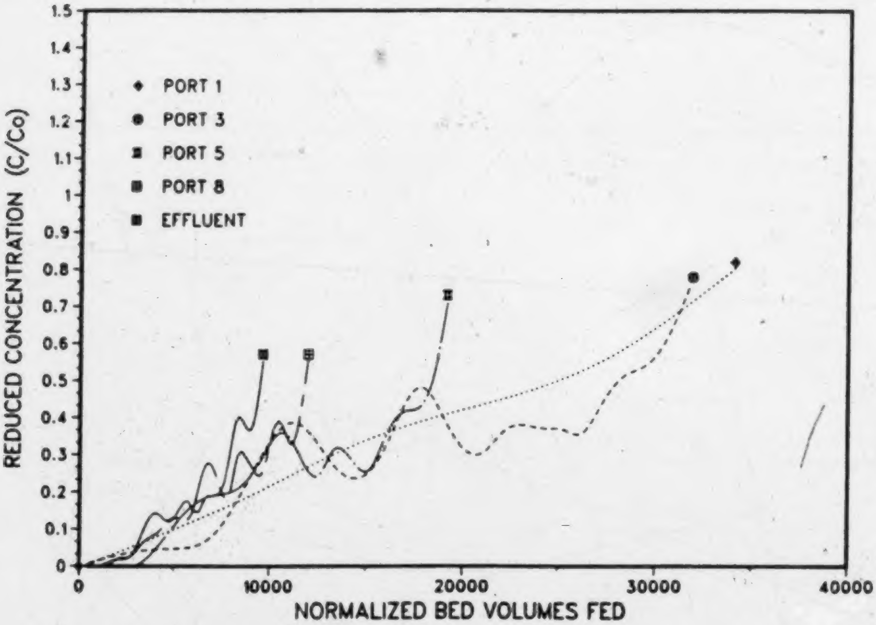


Figure 5.61 Reduced Concentration Bromodichloromethane Breakthrough Using Normalized Bed Volumes (1986 Ceca 830 Ported Bed)

was adsorbed more strongly than chloroform. A comparison of ECM breakthrough and overshoot predictions to actual data using various types of input data are shown in Figures 5.62 and 5.63, and in Appendix IX.

Bed volumes fed to breakthrough for full-scale segments 0-1 and 0-3 agreed well with ECM predictions using 4 to 8 week pre-loading parameters and HC's as input (Table 5.26). Breakthrough from a deeper bed as represented by segments 0-5, 0-8 and 0-effluent could not be represented by the model even when Freundlich parameters representing the maximum reduction in capacity were incorporated. Since influent concentrations of bromodichloromethane are lower than chloroform, the very low concentrations present at mid-column depth could partly account for the model's inability to predict breakthrough in the lower bed depths. Additional reasons would require further investigation.

Overshoot concentrations could not be directly compared with full-scale data since at no time during operation did effluent concentrations exceed influent concentrations for this compound. The ECM predictions using type IV input data appear to represent actual data if the breakthrough profiles can be assumed to continue at approximately the same slope.

In general ECM predictions for bromodichloromethane were not as good as for chloroform. However the usefulness of the ECM as a method of predicting THM breakthrough remains very strong since it should be recalled that chloroform represents 69% of the total contribution to TTHM's. It should also be noted that good predictions for chloroform were obtained despite the fact that reductions in

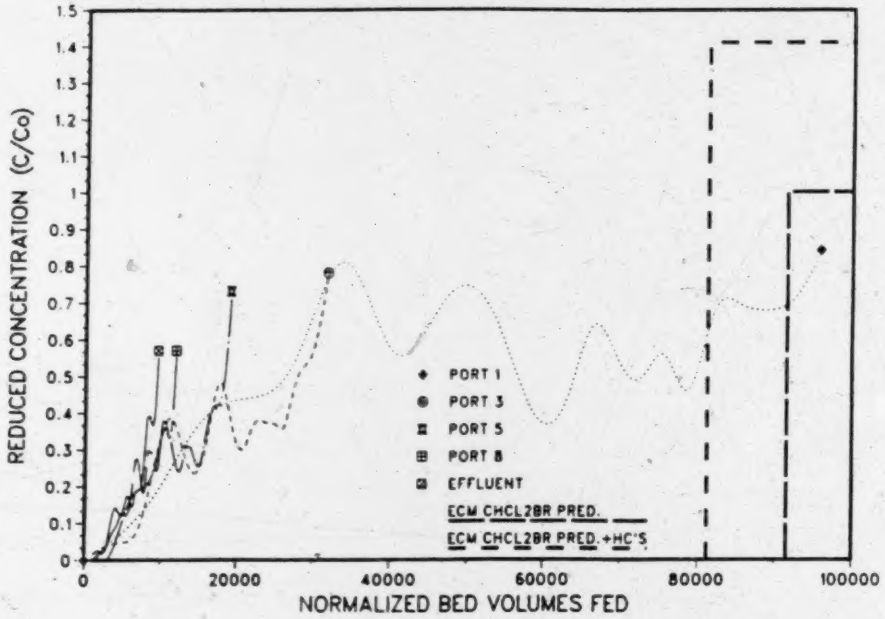


Figure 5.62 Effect of HC's on ECM Prediction of Bromodichloromethane Breakthrough (1986 Ceca 830 Ported Bed)

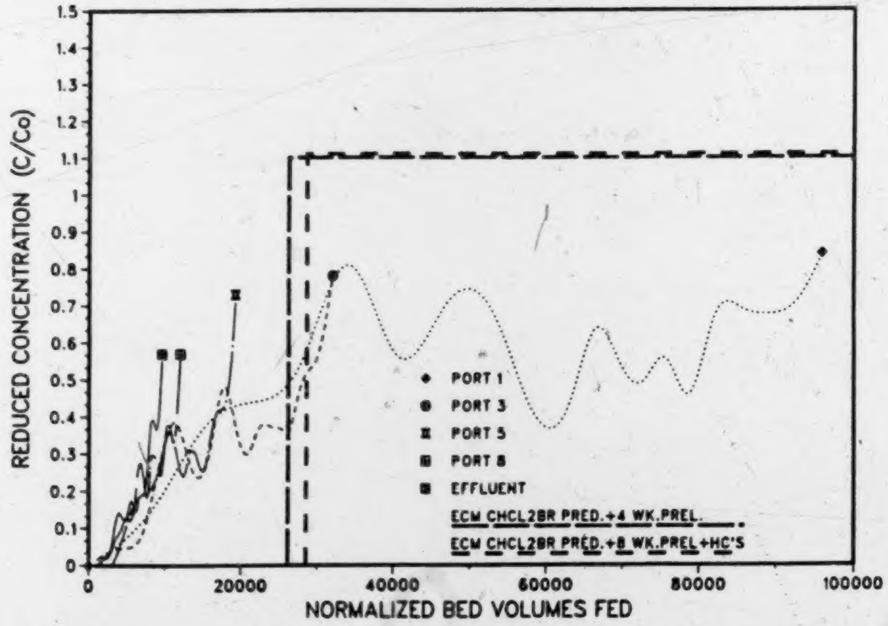


Figure 5.63 Effect of Pre-Loading Time and HC's on ECM Prediction of Bromodichloromethane Breakthrough (1986 Ceca 830 Ported Bed)

Table 5.26 Comparison of ECM Predictions to Full-Scale 1986 Bromodichloromethane Data for Ceca 830 Ported Contactor

Column Segment	Normalized Bed Volumes Fed to Breakthrough								
	Full Scale Bed (C/C_0=0.5)	ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0 - 1	26,530	91,546	81,195	67,026	60,778	26,160[a]	28,502	23,944	26,577[b]
0 - 3	28,170	91,546	81,195	67,026	60,778	26,160[a]	28,502	23,944	26,577[b]
0 - 5	18,420	91,546	81,195	67,026	60,778	26,160[a]	28,502	23,944	26,577[b]
0 - 8	11,270	91,546	81,195	67,026	60,778	26,160[a]	28,502	23,944	26,577[b]
0-Effl.	9,580	91,546	81,195	67,026	60,778	26,160[a]	28,502	23,944	26,577[b]

Actual full-scale operation time = 19.5 weeks

[a,b] BV fed to breakthrough exceeds value reported for earlier pre-loading time due to increase in Freundlich K parameter.

capacity due to pre-loading were estimated from the pre-loading experiments with F-300, and that regenerated carbon was used in the full scale bed whereas virgin carbon was used in the pre-loading tests. However, it must also be kept in mind that the pre-loading unavoidably included adsorption of THMs.

5.8.2.2.2 Filtrasorb 300® - 1986 Results

During 1986 full-scale GAC operation, regenerated Filtrasorb 300® carbon alone (not in combination with other carbons) was used in only one of the eight contactors. Since this contactor (number 8) was not equipped with monitoring ports, only effluent concentrations could be monitored.

Breakthrough profiles for chloroform and bromodichloromethane are shown in Figures 5.64 and 5.65, respectively. Neither profile displayed a reduced concentration equal to or greater than 1.0, indicating that total bed exhaustion had not been reached. This contactor however, was monitored for only 117 days following start-up as compared to the 139 day monitoring period for contactor number 3 which contained Ceca 830 and was discussed in Section 5.8.2.2.1.

The addition of HC's to input data for both single solute and two week pre-loaded Freundlich parameters caused a greater reduction in BVF to breakthrough for bromodichloromethane (Figures 5.68 and 5.69) than for chloroform (Figures 5.66 and 5.67). A similar type of shift was previously observed for the Ceca 830 carbon. The larger decrease in BVF for bromodichloromethane (the stronger adsorbing compound) was most likely attributable to its lower

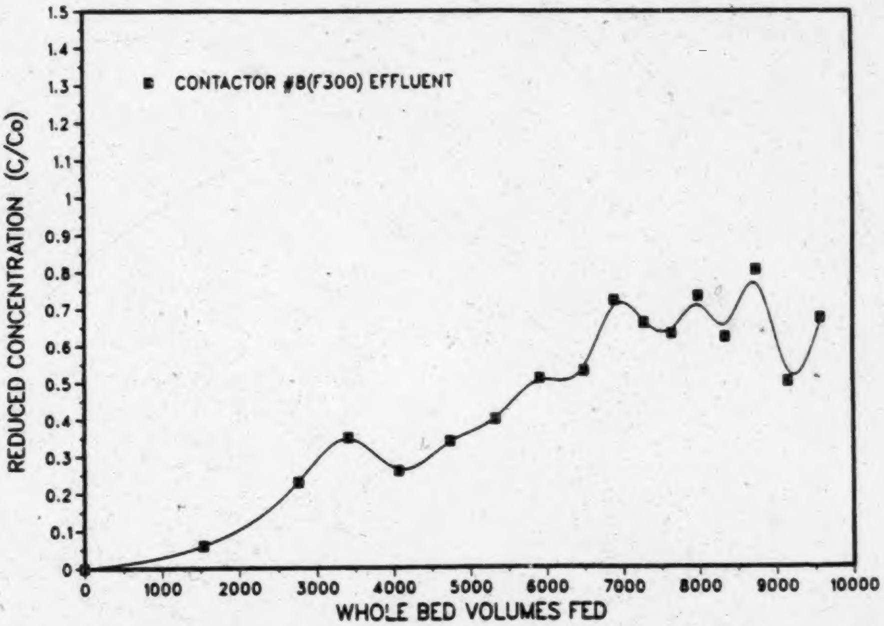


Figure 5.64 Reduced Concentration Chloroform Breakthrough (1986 Filtrasorb 300® Bed) (Adapted from Buffalo Pound Operating Data, 1986)

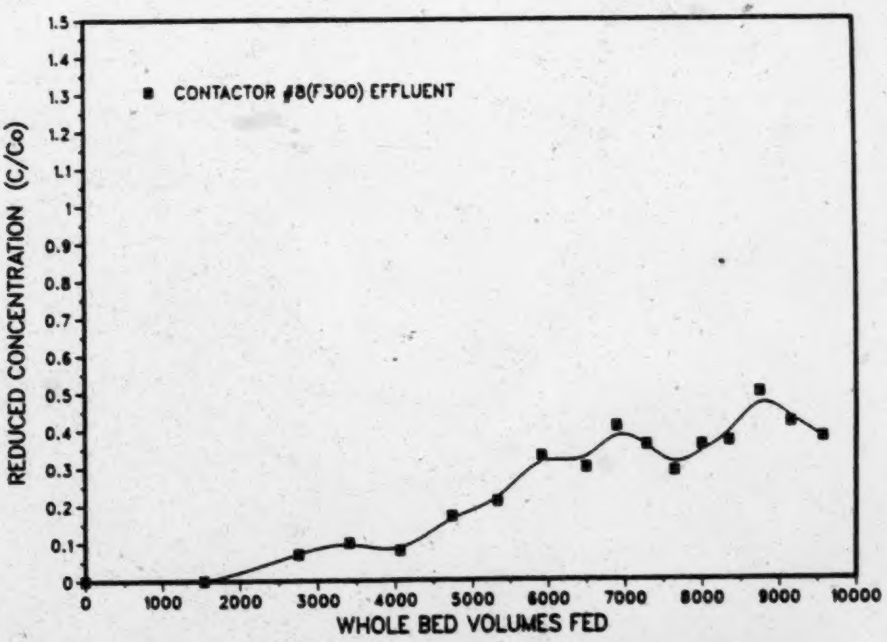


Figure 5.65 Reduced Concentration Bromodichloromethane Breakthrough (1986 Filtrasorb 300® Bed) (Adapted from Buffalo Pound Operating Data, 1986)

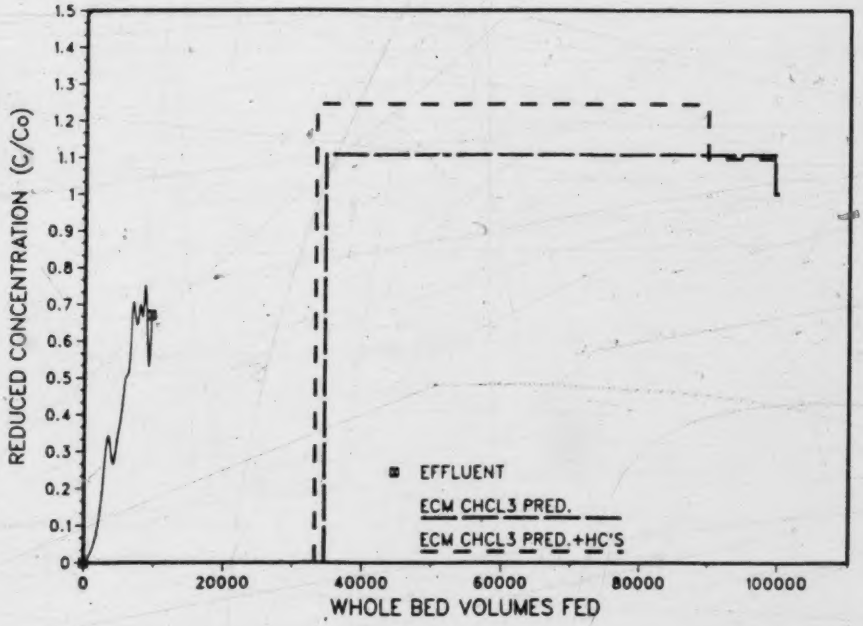


Figure 5.66 Effect of HC's on ECM Prediction of Chloroform Breakthrough (1986 Filtrasorb 300® Bed)

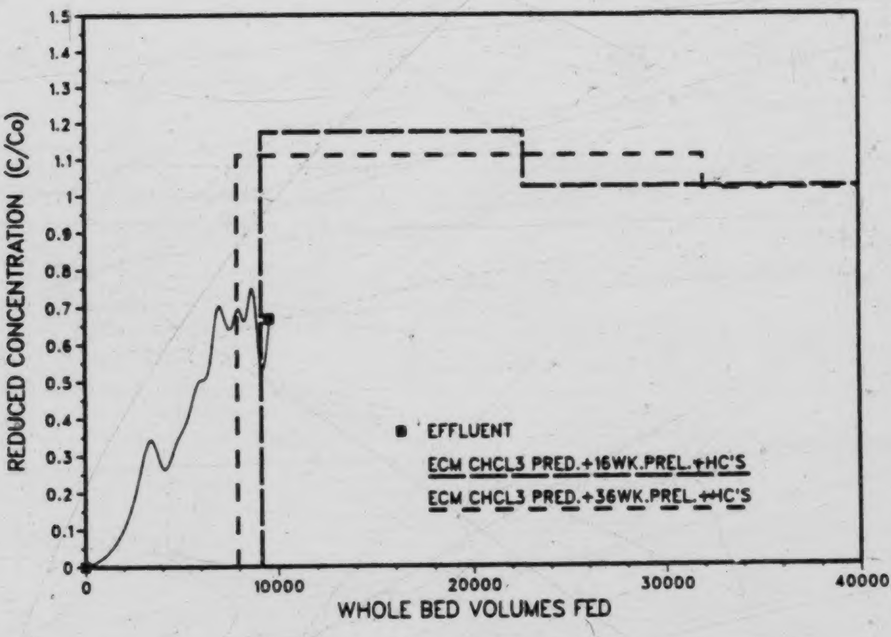


Figure 5.67 Effect of Pre-Loading Time and HC's on ECM Prediction of Chloroform Breakthrough (1986 Filtrasorb 300®)

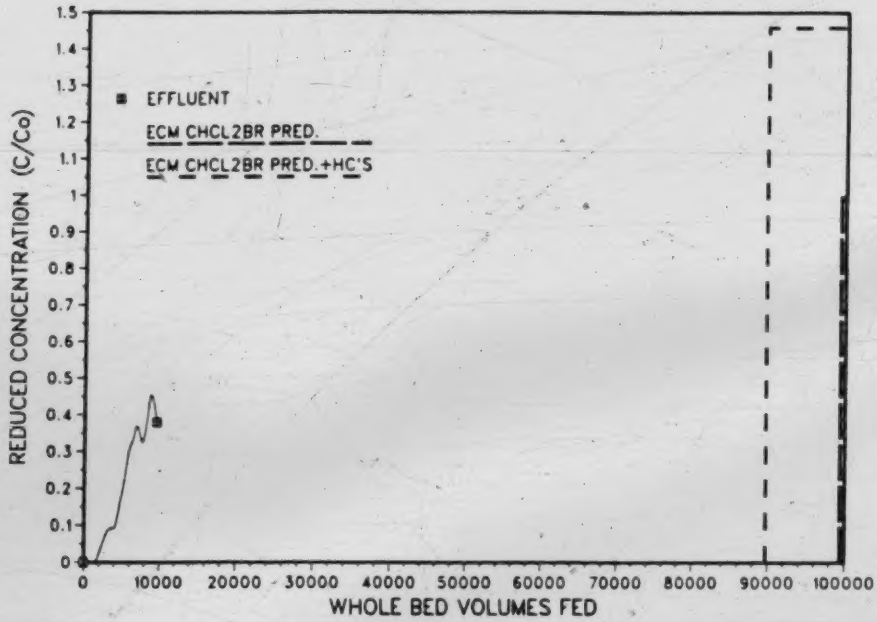


Figure 5.68 Effect of HC's on ECM Prediction of Bromodichloromethane Breakthrough (1986 Filtrasorb 300® Bed)

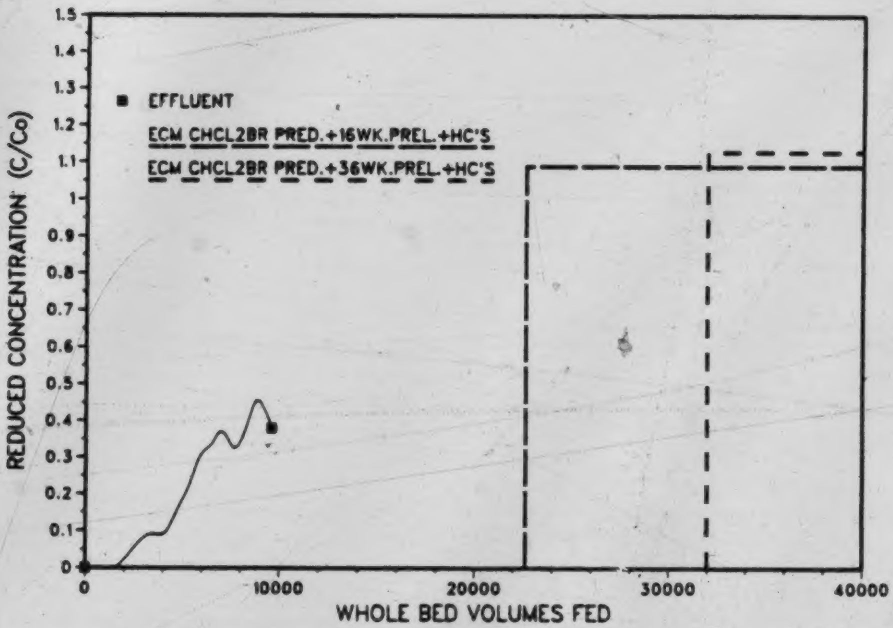


Figure 5.69 Effect of Pre-Loading Time and HC's on ECM Prediction of Bromodichloromethane Breakthrough (1986 Filtrasorb 300® Bed)

influent concentration. During the full-scale operating period an average bromodichloromethane concentration of 9.6 μg/L represented only 33% of the concentration reported for chloroform.

BVF to breakthrough are summarized for both compounds in Table 5.27. Breakthrough for chloroform was predicted more accurately than for bromodichloromethane. Using type IV data at a pre-loading time of 36 weeks, BVF to a reduced influent concentration of 0.5 (5960 BV) represented 75% of the predicted value (7928 BV). For bromodichloromethane an extrapolated breakthrough at 10,140 BV was approximately 45% of the value (22,630 BV) predicted using 16 week pre-loading parameters. As noted for the Ceca 830 carbon, breakthrough of bromodichloromethane was very gradual suggesting that a wide mass transfer zone exists for this compound. Since ECM predictions ignore mass transfer influences, predictions for this compound were expected to be less accurate than for those observed for chloroform.

5.8.2.3 Comparison of 1986 THM Breakthrough Data

To allow breakthrough predictions to be readily applied to Buffalo Pound, the two contactors used in comparative discussions must be representative of other contactors which were not as intensely monitored. Figures 5.70 and 5.71 respectively show chloroform and bromodichloromethane breakthrough profiles for four of the eight full-scale contactors which were operated at Buffalo Pound during 1986. Contactors not represented in the plot either were operated intermittently, contained mixtures of carbon, or were not monitored in sufficient detail.

Table 5.27 Comparison of ECM Breakthrough to Full-Scale 1986 Data for Filtrasorb-300® Contactor

(a) Chloroform

Column Segment	Full Scale Bed (C/C_0=0.5)	Normalized Bed Volumes Fed to Breakthrough							
		ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0-Effl.	5,960	34,572	33,228	14,215	14,054	9,982	8,814	9,166[a]	7,928

Actual full-scale operating time = 19.9 weeks

[a] The 16 week BVF to breakthrough exceeds those reported for 8 weeks due to differences in pre-loaded Freundlich parameters.

(b) Bromodichloromethane

Column Segment	Full Scale Bed (C/C_0=0.5)	Normalized Bed Volumes Fed to Breakthrough							
		ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0-Effl.	10,140	99,366	89,740	62,636	56,870	20,956	30,900[a]	22,630	31,973[b]

Actual full-scale operating time = 19.9 weeks

[a,b] BV fed to breakthrough exceeds value reported for earlier pre-loading time due to increase in Freundlich K parameter.

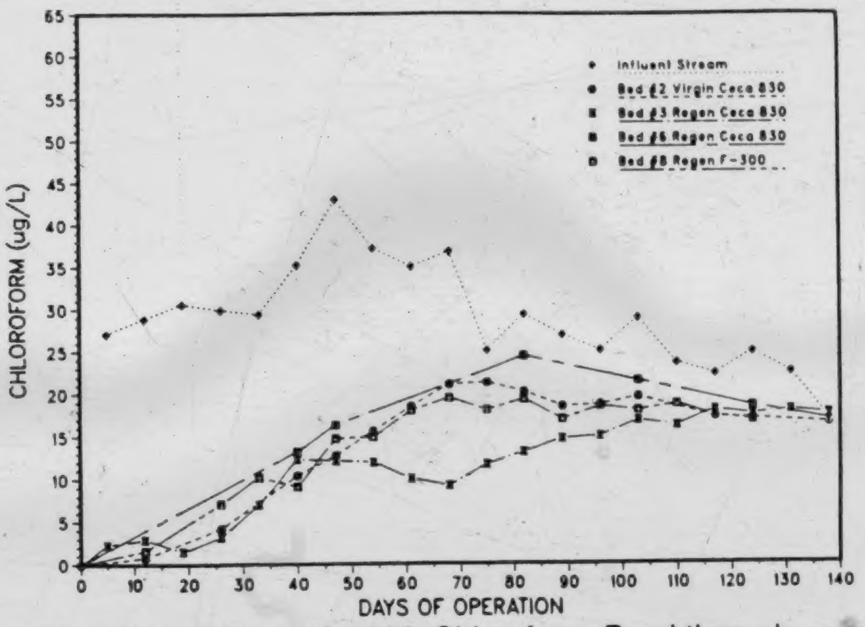


Figure 5.70 Comparison of 1986 Chloroform Breakthrough versus Time for Full-Scale Contactors (Adapted from Buffalo Pound Operating Data, 1986)

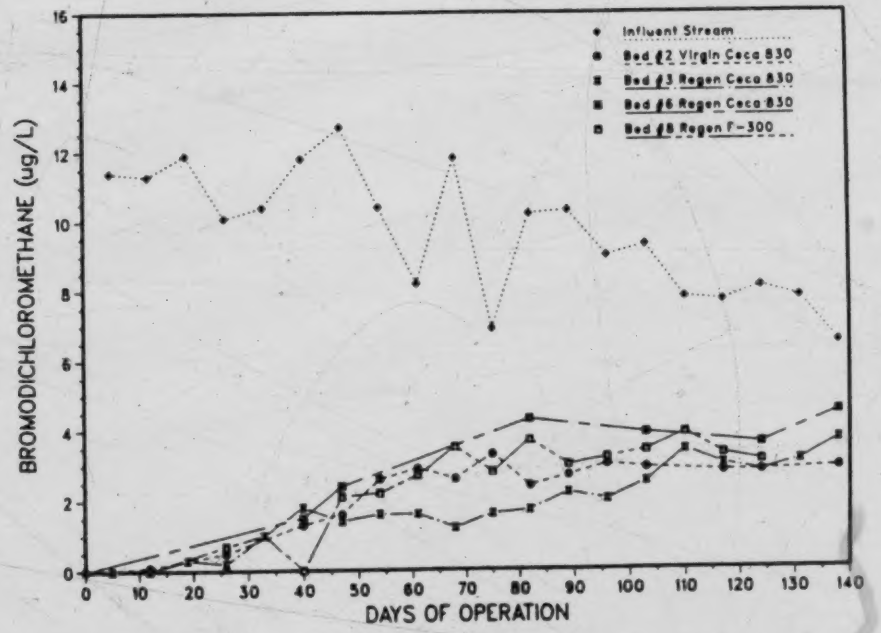


Figure 5.71 Comparison of 1986 Bromodichloromethane Breakthrough versus Time for Full-Scale Contactors (Adapted from Buffalo Pound Operating Data, 1986)

Contactors numbered 3 and 8 (Figures 5.70 and 5.71) were used to represent the Ceca 830 and Filtrasorb 300® carbons, respectively. The regenerated Ceca 830 breakthrough profile (contactor 3) compared well for both chloroform and bromodichloromethane with virgin Ceca 830 carbon (contactor 2), regenerated Filtrasorb 300® (contactor 8) and a similar bed containing regenerated Ceca 830 carbon, especially at the beginning and end of the operating period. At day 59, 56 cm of regenerated carbon was added to the top of contactor 3 in an attempt to extend the operating time to breakthrough for taste and odour causing compounds. This addition of carbon caused a reduction in THM effluent concentrations as shown by the divergence in breakthrough curves from days 60 to 100. This addition was accounted for by applying a correction to BVF calculations which applied to contactor 3 only. Figures 5.72 and 5.73 respectively show chloroform and bromodichloromethane plotted versus bed volumes. These plots confirm that the beds studied in detail were indeed representative of other full-scale contactors up to day 59.

5.8.2.4 Filtrasorb 300® Ported Bed - 1987 Results

Prior to the 1987 GAC operating season, regenerated Filtrasorb 300® was placed in the contactor 3 which was equipped with monitoring ports to enable breakthrough profiles to be constructed for various bed depths. Breakthrough profiles for chloroform before and after normalization are shown in Figures 5.74 and 5.75, respectively. The influent concentration averaged 32.0±7.6 µg/L, with a slight decreasing trend during the operation period.

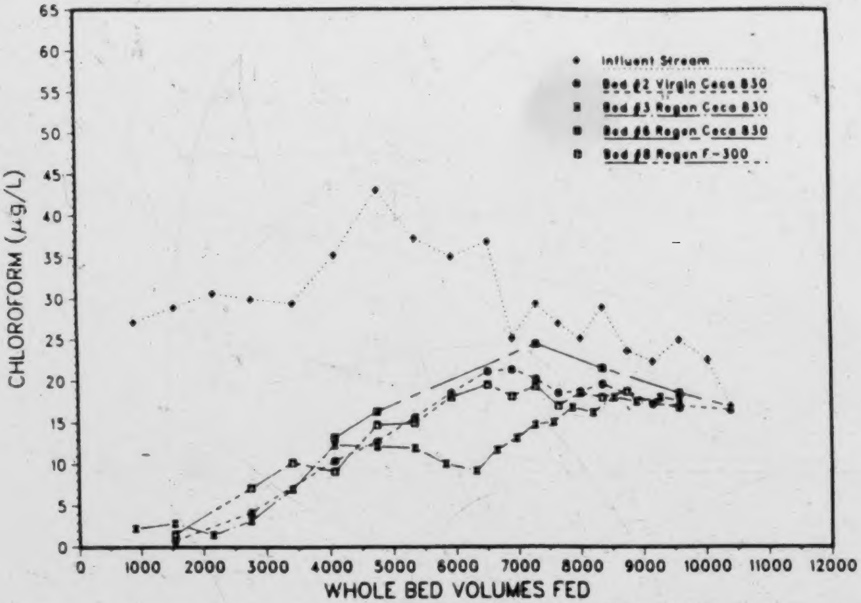


Figure 5.72 Comparison of 1986 Chloroform Breakthrough versus Bed Volumes for Full-Scale Contactors (Adapted from Buffalo Pound Operating Data, 1986)

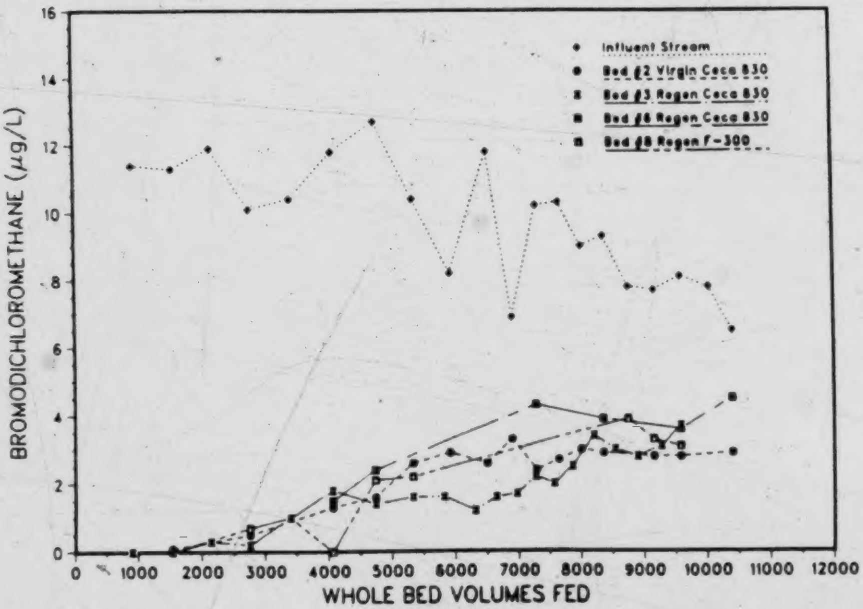


Figure 5.73 Comparison of 1986 Bromodichloromethane Breakthrough versus Bed Volumes for Full-Scale Contactors (Adapted from Buffalo Pound Operating Data, 1986)

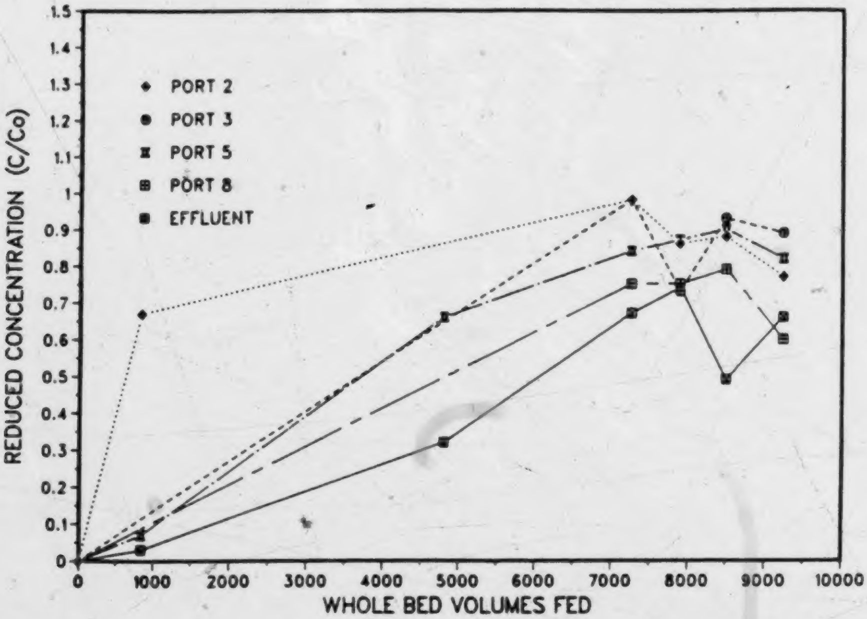


Figure 5.74 Reduced Concentration Chloroform Breakthrough (1987 Filtrasorb 300® Ported Bed)

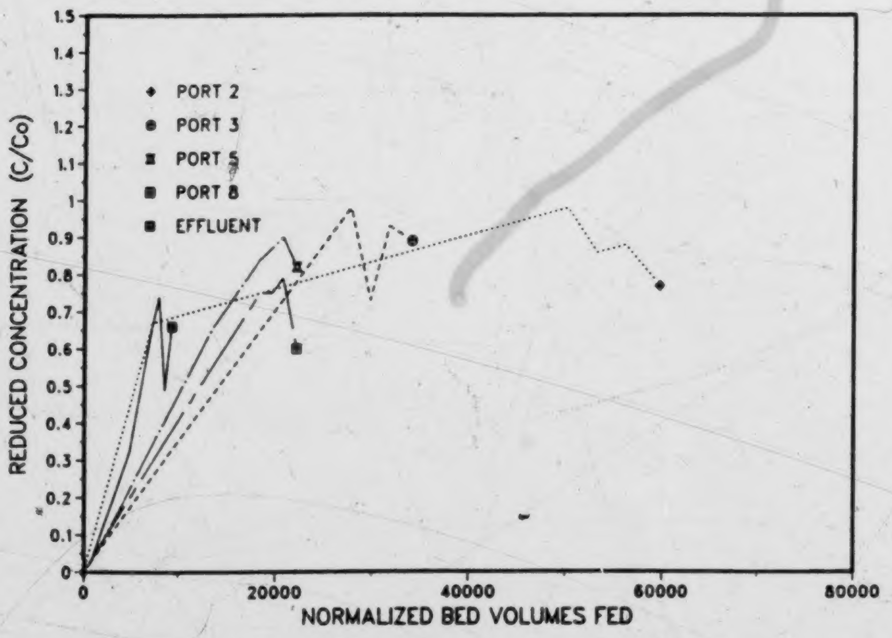


Figure 5.75 Reduced Concentration Chloroform Breakthrough Using Normalized Bed Volumes (1987 Filtrasorb 300® Ported Bed)

Comparisons of chloroform ECM breakthrough predictions to full-scale results are shown in Figures 5.76 and 5.77.

Breakthrough data collected for the full-scale bed segment 0-2 appeared anomalous when compared to previous data collected for other beds (Table 5.28). The low value obtained for BVF to breakthrough may be attributed to a lack of sufficient concentration data obtained at port 2 immediately following start-up of the contactor. Also, the irregular breakthrough pattern observed at various contactor depths should not be judged as significant due to a similar lack of concentration data for the first 7,000 bed volumes.

BVF to breakthrough values obtained for segments 0-3 and 0-5 agreed well with ECM predictions using type IV data and 2 and 4 week pre-loading times respectively. Four week pre-loading data was also used to obtain the most accurate ECM BVF estimates for the Ceca 830 0-5 segment during 1986. A sharp decrease in BVF to breakthrough was observed in the lowest 0.6 m of bed depth as illustrated using the 0-8 and 0-effluent segments. This suggests that the carbon capacity near the bottom of the bed was greatly influenced by pre-loading. ECM estimates of BVF to breakthrough for segment 0-effluent, representing the entire bed would require that a pre-loading time of 8 weeks or greater be used in type IV input data to the model. Overshoot predictions could not be related directly to observed results since saturation did not occur during the 14 week operating period.

Breakthrough profiles for bromodichloromethane before and after normalization are shown in Figures 5.78 and 5.79, respectively. As for chloroform the influent concentration decreased slightly

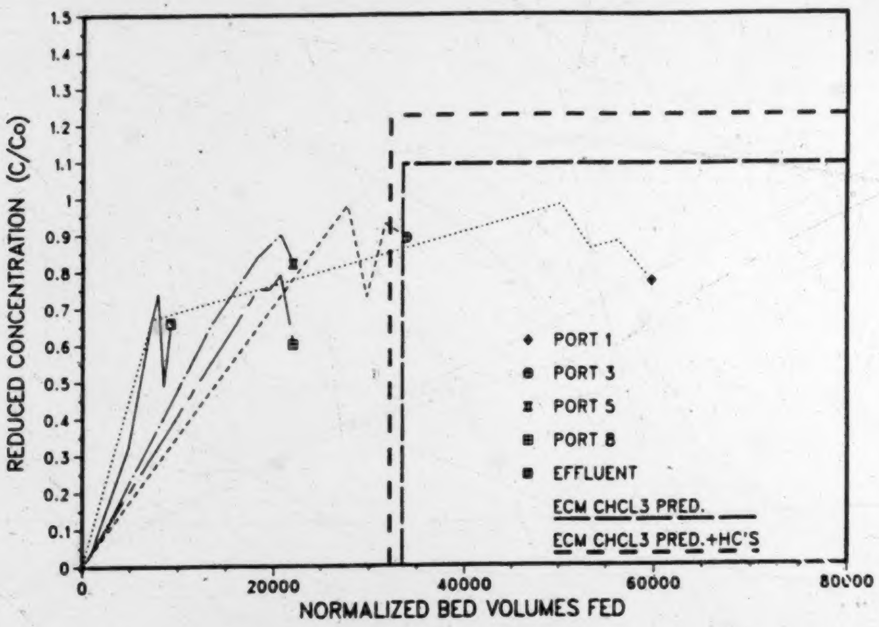


Figure 5.76 Effect of HC's on ECM Prediction of Chloroform Breakthrough (1987 Filtrasorb 300® Ported Bed)

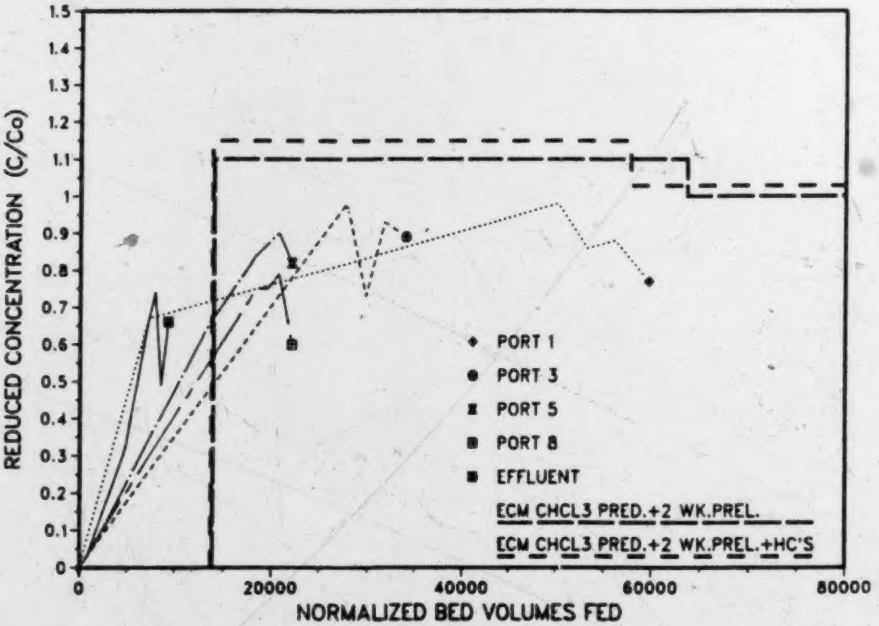


Figure 5.77 Effect of Pre-Loading Time and HC's on ECM Prediction of Chloroform Breakthrough (1987 Filtrasorb 300® Ported Bed)

Table 5.28 Comparison of ECM Predictions to Full-Scale 1987 Chloroform Data for Filtrasorb 300® Ported Contactor

Column Segment	Full Scale Bed (C/C_0=0.5)	Normalized Bed Volumes Fed to Breakthrough							
		ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0 - 2	5,393[a]	33,549	32,280	13,891	13,739	9,661	8,643	8,910[b]	7,766
0 - 3	14,157	33,549	32,280	13,891	13,739	9,661	8,643	8,910[b]	7,766
0 - 5	10,337	33,549	32,280	13,891	13,739	9,661	8,643	8,910[b]	7,766
0 - 8	12,135	33,549	32,280	13,891	13,739	9,661	8,643	8,910[b]	7,766
0-Effl.	6,067	33,549	32,280	13,891	13,739	9,661	8,643	8,910[b]	7,766

Actual full-scale operation time = 14.4 weeks

[a] Appears anomalous due to lack of sufficient concentration data immediately following contactor start-up

[b] BV fed to breakthrough exceeds value reported for previous pre-loading time due to increase in Freundlich K parameter

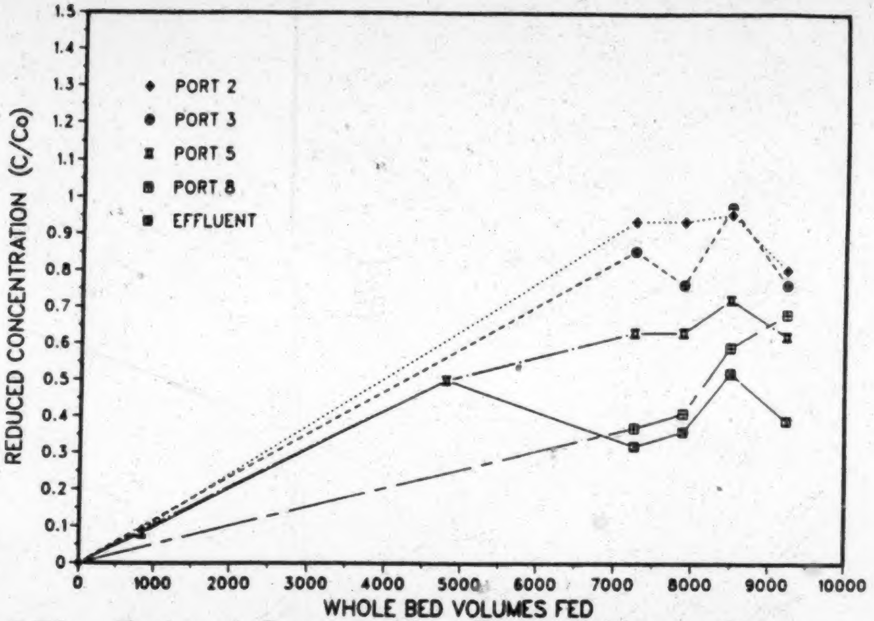


Figure 5.78 Reduced Concentration Bromodichloromethane Breakthrough (1987 Filtrasorb 300® Ported Bed) (Adapted from Buffalo Pound Operating Data, 1987)

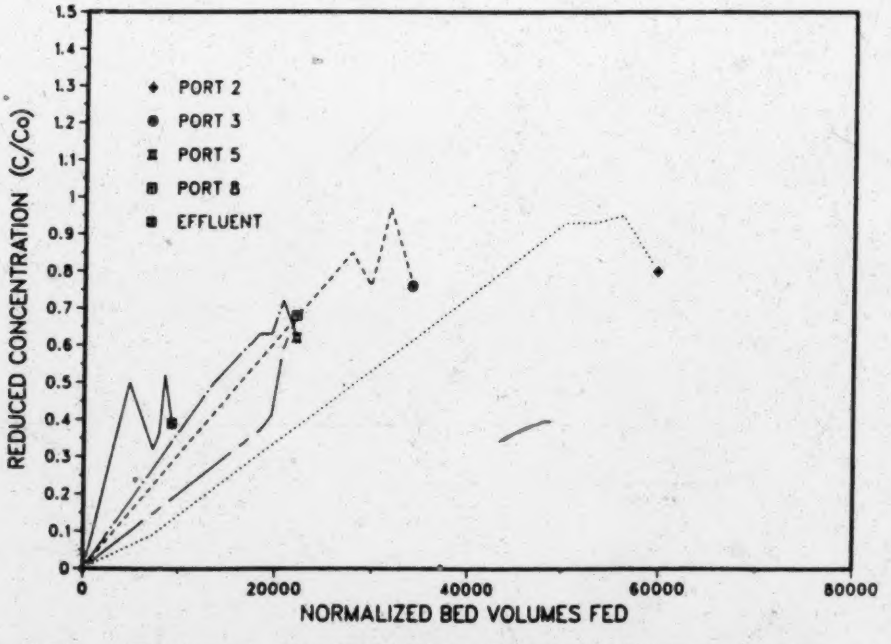


Figure 5.79 Reduced Concentration Bromodichloromethane Breakthrough Using Normalized Bed Volumes (1987 Filtrasorb 300® Ported Bed) (Adapted from Buffalo Pound Operating Data, 1987)

during the operating period, averaging 9.1±2.6 µg/L. ECM breakthrough predictions are shown in Figures 5.80 and 5.81.

Results are summarized in Table 5.29. In general breakthrough for segments extending to 80% of the full-scale bed depth (segment 0-8) could be predicted using 4 week pre-loaded input data. As for chloroform, the BVF to breakthrough at the full bed depth (segment 0-effluent) was over-estimated by the ECM. This observation again suggested a that a large reduction in capacity existed near the bottom of the contactor.

5.9 SUMMARY

Single solute adsorption isotherms were conducted for chloroform, bromodichloromethane, dibromochloromethane and bromoform on three commercially available activated carbons, two of which, Filtrasorb 300® and Ceca 830, were used in the full scale GAC treatment process at Buffalo Pound. The third carbon, Filtrasorb 400®, served as an alternative carbon to provide comparative data. Equilibrium capacities for chloroform, bromodichloromethane, dibromochloromethane and bromoform were shown to be highest for the F-300 carbon.

Experiments involving two and four component mixtures of THM's were used to verify that IAST could be used to predict equilibrium behaviour in known mixtures at low concentration levels. For the two carbons used at the Buffalo Pound water treatment plant, experimentally obtained data points compared well to model predictions although IAST tended to slightly underestimate competitive displacement for two component mixtures.

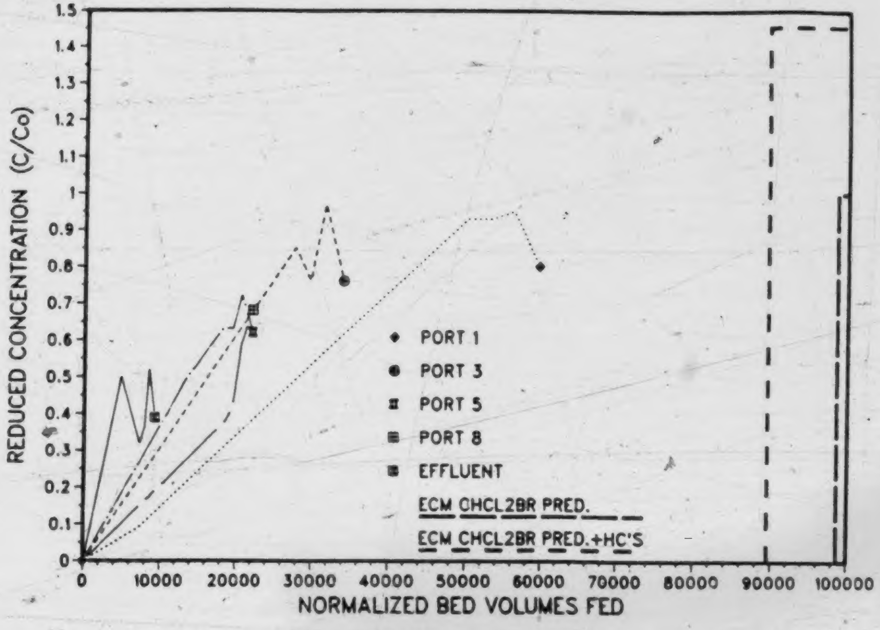


Figure 5.80 Effect of HC's on ECM Prediction of Bromodichloromethane Breakthrough (1987 Filtrasorb 300® Ported Bed)

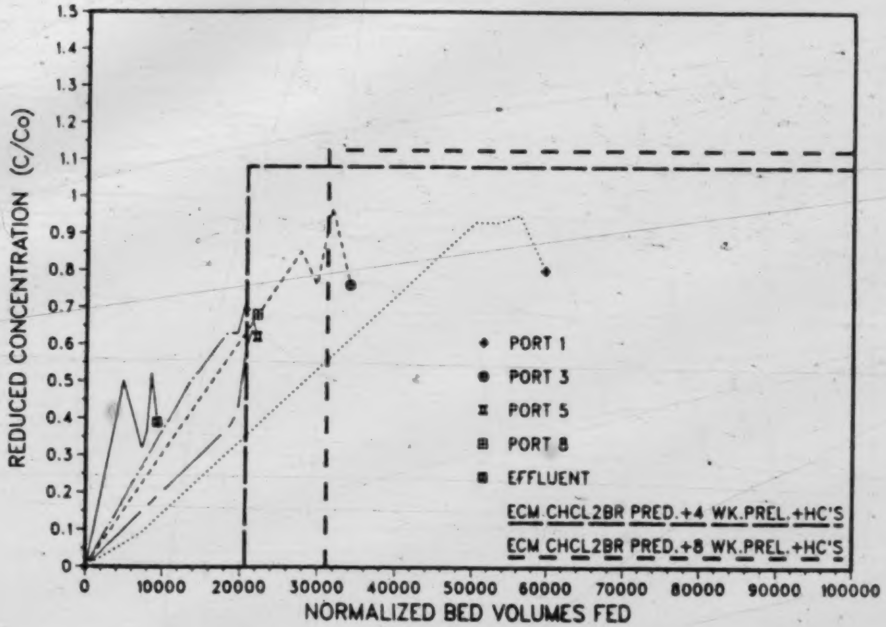


Figure 5.81 Effect of Pre-Loading Time and HC's on ECM Prediction of Bromodichloromethane Breakthrough (1987 Filtrasorb 300® Ported Bed)

Table 5.29 Comparison of ECM Predictions to Full-Scale 1987 Bromodichloromethane Data for Filtrasorb 300® Ported Contactor

	Normalized Bed Volumes Fed to Breakthrough								
Column Segment	Full Scale Bed (C/C_0=0.5)	ECM Predictions (Input Data Type)							
		I	II	III	IV (Weeks of Pre-loading)				
					2	4	8	16	36
0 - 2	29,014	98,652	89,535	63,592	57,771	20,676	31,139[a]	22,483	32,193[a]
0 - 3	16,620	98,652	89,535	63,592	57,771	20,676	31,139[a]	22,483	32,193[a]
0 - 5	13,803	98,652	89,535	63,592	57,771	20,676	31,139[a]	22,483	32,193[a]
0 - 8	20,282	98,652	89,535	63,592	57,771	20,676	31,139[a]	22,483	32,193[a]
0-Effl.	8,451	98,652	89,535	63,592	57,771	20,676	31,139[a]	22,483	32,193[a]

Actual full-scale operation time = 14.4 weeks

[a] BV fed to breakthrough exceeds value reported for previous pre-loading time due to increase in Freundlich K parameter

Isotherm experiments allowed competition due to the co-adsorption of unidentified "background" organics to be evaluated. IAST predictions using HC's simulated the downward displacement in isotherms due to background competition, and provided good agreement between observed and predicted data.

The general applicability of using HC's to predict isotherm displacement was assessed for four different water matrices using averaged HC values to represent the GAC operating period. Results illustrated that determinations of unique HC values were not required to represent background competition for a given time during the full-scale GAC adsorber operating season at Buffalo Pound. The relative adsorbability of any THM compound of interest may therefore be calculated by knowing only its single solute parameter values and an approximate representation of background competition as defined by HC's. However, background competition during a severe algal bloom, or during winter (if the contactors were to be operating then) might not be adequately predicted by this approach.

A pre-loading column was used to evaluate the reduction of THM capacity at Buffalo Pound attributable to pre-loading of carbon with background organics. For procedural reasons, some THMs were unavoidably adsorbed along with the background organics. This pre-loaded carbon served to represent the carbon present in lower segments of the full-scale GAC beds where slow fouling with background organics occurs prior to adsorption of THMs. Isotherm experiments provided estimates of Freundlich parameters for chloroform and bromodichlormethane on pre-loaded carbon. A reduction in the Freundlich K parameter was observed to occur as the pre-loading time increased. This observation was consistent with earlier findings of Zimmer et al. (1987a) for trichloroethene, 1,1,1-trichloroethane, and tetrachoroethene on Filtrasorb 100® (similar to Filtrasorb 100®) pre-loaded with Karlsruhe, West Germany tap water.

To determine if the reduction in adsorptive capacity (Freundlich K) could be related to the other parameters which define the background organic loading present on the carbon, TOX analyses were conducted on individual pre-loaded carbon samples. When the reduction in K was compared to accumulated TOX, an inverse relationship was observed. Therefore, for a given compound such as chloroform it may be possible to relate residual adsorptive capacity to pre-adsorbed TOX. To confirm a hypothesis of this type however would require further study using other compounds of varying adsorptive strengths, different carbons, and various water matrices.

Equilibrium Column Model (ECM) predictions were compared to full-scale contactor results for both the 1986 and 1987 operating periods. In order to examine the overall usefulness of the ECM, which ignores mass transfer resistances, Freundlich parameters used as input data included single solute isotherm results, pre-loaded carbon isotherm results, and hypothetical components (HC's), in various combinations. A very good agreement between ECM predicted BVF to breakthrough, and the midpoint in actual breakthrough curves was noted for chloroform when the model incorporated Freundlich parameters revised to account for capacity reduction due to pre-loading. The overshoot concentration obtained immediately prior to full-scale contactor shutdown also agreed well with ECM predictions. Breakthrough predictions were less successful for bromodichloromethane especially in the lower half of the full-scale bed.

This research demonstrated that, to estimate GAC capacity for trihalomethanes in an actual water treatment plant application, the effects of background competition and pre-loading with background organics must be accounted for. In this investigation, the influence of co-adsorption of background organics was of much less significance. The results illustrated that simple computer models may be applied to provide estimates of GAC capacity and breakthrough in full-scale contactors provided that adequate input data, reflecting actual treatment conditions is utilized.

6.0 QUANTITATION OF THE REMOVAL OF THE MUTAGENIC COMPOUND 'MX' FROM DRINKING WATER BY ACTIVATED CARBON

The use of activated carbon in water treatment has been shown to be an effective means of removing mutagenicity produced during chlorination of drinking water. While mutagenicity is not currently a regulated parameter and a direct connection cannot be made between mutagenic potential and human health, the demonstrated correlation between mutagenicity and carcinogenicity for certain compounds (e.g. Monarca et al., 1983) suggests that it would be prudent to minimize its occurrence in drinking water. This chapter evaluates the formation and removal of mutagenicity at various water treatment facilities by focussing on the potent mutagen MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone].

The adsorptive potential of activated carbon to remove MX was examined using isotherms in a similar manner to that described for trihalomethanes in Chapter 5. Data was also collected concerning reduction in capacity attributable to pre-loading with background organics. To illustrate that an adsorption mechanism was involved, several combinations of solvents and desorption conditions were examined for recovery of pre-adsorbed MX from activated carbon. To establish the relative removal of mutagenicity as represented by MX using GAC to other more commonly monitored compounds such as THM, this chapter provides comparisons based on both experimentally determined data and computer model predictions.

6.1 GC/MS Evaluation of Synthesized MX

Following evaluation of two competing bids, the University of Alberta Chemistry Department was subcontracted to synthesize 1.5 g of MX. The method used was that described by Padmapriya et al., (1985) with several slight changes reflecting modifications by Christman (1988). In early July 1988 the first delivery was received. This consisted of approximately 10 mg of MX along with an undetermined amount of a synthesis byproduct believed to be an impurity.

An IR spectrum (Figure X.1, Appendix X) which accompanied the sample corresponded well to that reported for MX in the literature (Padmapriya et al., 1985). To determine the exact mass of the MX crystals received, they were dissolved in a small volume of ethyl acetate, transferred to a clean, dry, pre-weighed vial and the solvent evaporated under a gentle stream of nitrogen. The mass of the vial plus MX, minus the mass of the vial alone resulted in a mass of MX of 9.8 mg. The MX was re-dissolved in ethyl acetate and split into 2 portions for storage at 4°C in the dark. GC/MS analyses were subsequently conducted to determine the purity of the synthesized product.

6.1.1 Total and Selected Ion Current Results

On September 9, 1988 approximately 549 mg of MX without impurities was received. Fresh working standards were prepared and stored at 4°C in ethyl acetate. GC/ECD analysis of derivatives of these solutions showed that the area ratios of MX to EMX were 34.5:1 (97.2% MX; 2.9% EMX).

GC/MS analysis of one derivatized solution containing 5 mg MX+EMX substantiated the GC/ECD results. Table X.1 (Appendix X) lists the GC/MS numerical data, whereas Figure X.2 (Appendix X) shows the entire TIC chromatogram for the analysis and indicates that the few decomposition products observed were present in relatively low concentrations. Figure X.3 (Appendix X) shows the mass spectra of the peaks observed and Figure X.4 (Appendix X) shows the single ion current chromatograms for ions m/e 201, 245 and 241 (indicative of MX, EMX and MBA respectively) and the ion area determinations of each ion peak. Calculations using these data and response factors reported by Kronberg et al. (1988) show that the ratio of MX to EMX in this solution was 31.1:1. Prior to conducting quantitive experiments with the MX, the ratio of MX to EMX was determined by GC/MS and used as a correction in the analysis of standards by GC/ECD.

A complete discussion concerning optimization of the derivatization procedure and internal standard reproducibility is presented in Appendix XI.

6.1.2 Analysis of Underivatized MX

2μL of the stock MX received (underivatized in ethyl acetate) were analyzed by direct MS analysis using a probe which could be temperature programmed and inserted directly into the ionization chamber of the mass spectrometer. Temperature programming the probe from ambient to 300°C at 3°C/min showed only one peak, the mass spectrum of which is shown in Figure X.5 (Appendix X). This mass spectrum compares very favourably to that published for underivatized MX (Padmapriya et al., 1985). The ion at m/e 180 may indicate the presence of some EMX, but from relative ion abundances, the amount is very small. (Absolute response factors for this ion were unavailable.)

6.2 MX/EMX Quantitation for Various Water Treatment Plants

Six Canadian water treatment plants were selected to evaluate the occurrence and removal of MX. Excluding Plant B all plants selected were chosen because of high influent TOC concentrations and/or the use of a pre-chlorination step (Andrews et al., 1990).

6.2.1 Individual Water Treatment Plant Characteristics

Specific information concerning the water treatment plants selected is presented in Table 6.1. All treat surface water and the raw water pH ranged from 7.4 to 8.1. In all but one instance water temperature was below 5°C at the time of sampling. Raw water TOC values ranged from a low of 2.7 mg/L for Plant B to a high of 27.1 mg/L for Plant E.

Plants A and C practice both pre-chlorination and post-chlorination. Plants D and F employ post-chlorination only while Plant E employs post-chloramination. Plant B uses chlorine dioxide and chloramines, however this plant was only sampled at the raw water position. Both plants A and C include GAC treatment, but at plant A the GAC was off-line at the time of the sampling. Complete schematics for plants A, C, D, E and F are shown in Figures 6.1, 6.2, 6.3, 6.4 and 6.5 respectively.

Table 6.1 Individual Treatment Plant Characteristics

Sample Location and Date	Water Source	Disinfection Scheme (b)	Selected Raw Water Characteristics		
			Temperature (°C) (a)	pH (a)	TOC (mg/L)
Plant A (Dec. 21/88)	Surface	Cl2-Cl2	4.6	8.1	4.9
(Jan. 24/89)	"	"	4.5	7.6	4.2
Plant B (Dec. 16/88)	Surface	ClO2-NH2Cl	7.0	7.9	2.7
Plant C (Jan. 09/89)	Surface	Cl2-(GAC)-Cl2	4.6	7.7	15.9
(Jan. 23/89)	"	"	3.8	7.4	13.5
Plant D (Jan. 12/89)	Surface	-Cl2	3.0	8.0	17.0
Plant E (Jan. 16/89)	Surface	-NH2Cl	4.1	7.6	27.1
Plant F (Jan. 19/89)	Surface	-Cl2	4.0	7.6	24.1

(a) Measured at time of sample collection.

(b) Cl2-Cl2=pre and post chlorination, Cl2-(GAC)-Cl2=pre chlorination; GAC prior to post chlorination -Cl2=post chlorination only, ClO2-NH2Cl=chlorine dioxide+chloramination, -NH2Cl=post chloramination only

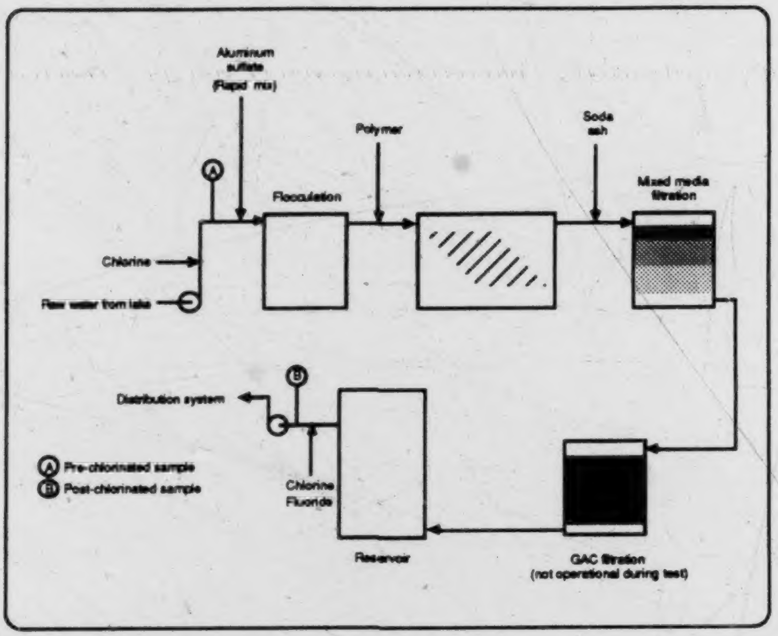

Aluminum sulfate (Rapid mix)
Polymer
Soda ash
Flocculation
Mixed media filtration
Chlorine
Raw water from lake
A
B
Distribution system
Chlorine Fluoride
Reservoir
GAC filtration (not operational during test)
A Pre-chlorinated sample
B Post-chlorinated sample

Figure 6.1 Treatment Plant Schematic - Plant A

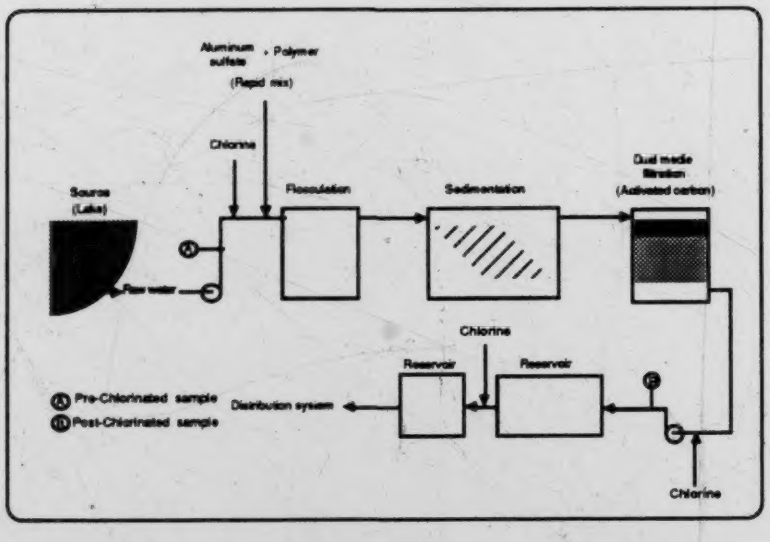

Aluminum sulfate + Polymer
(Rapid mix)
Chlorine
Source (Lake)
Flocculation
Sedimentation
Dual media filtration (Activated carbon)
A
Raw water
Chlorine
Reservoir
Reservoir
B
Distribution system
Chlorine
A Pre-Chlorinated sample
B Post-Chlorinated sample

Figure 6.2 Treatment Plant Schematic - Plant C

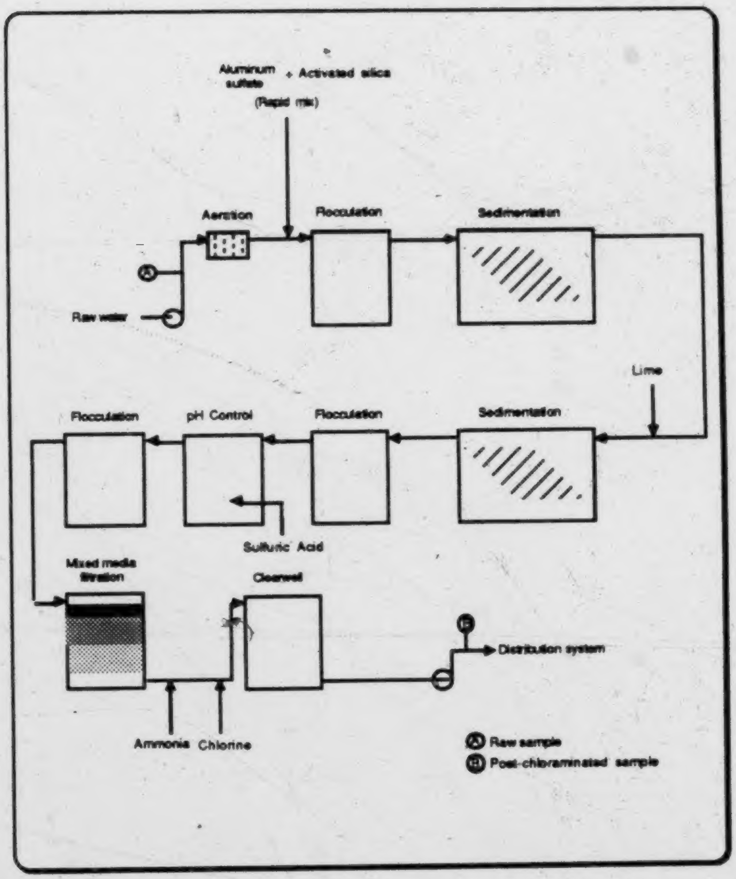

Aluminum sulfate + Activated silica
(Rapid mix)
Aeration
Flocculation
Sedimentation
A
Raw water
Lime
Flocculation
pH Control
Flocculation
Sedimentation
Sulfuric Acid
Mixed media filtration
Clearwell
B
Distribution system
Ammonia
Chlorine
A Raw sample
B Post-chloraminated sample

Figure 6.3 Treatment Plant Schematic - Plant D

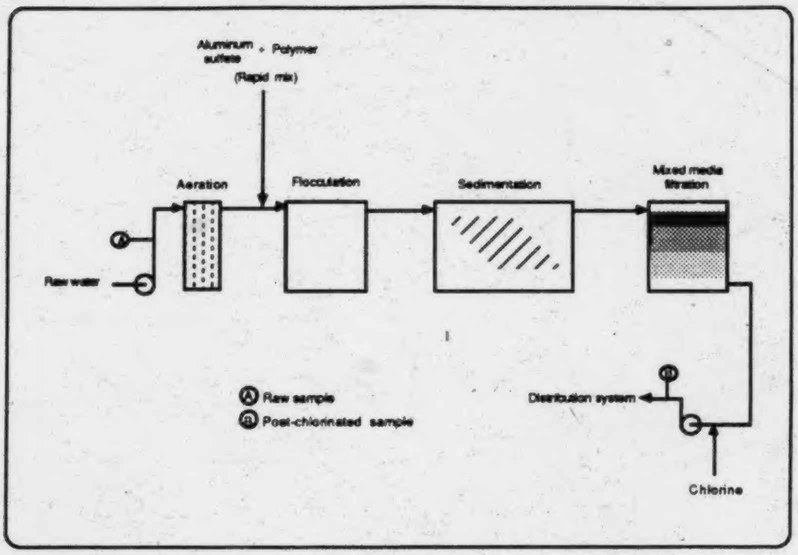

Aluminum sulfate + Polymer
(Rapid mix)
Aeration
Flocculation
Sedimentation
Mixed media filtration
A
Raw water
B
A Raw sample
B Post-chlorinated sample
Distribution system
Chlorine

Figure 6.4 Treatment Plant Schematic - Plant E

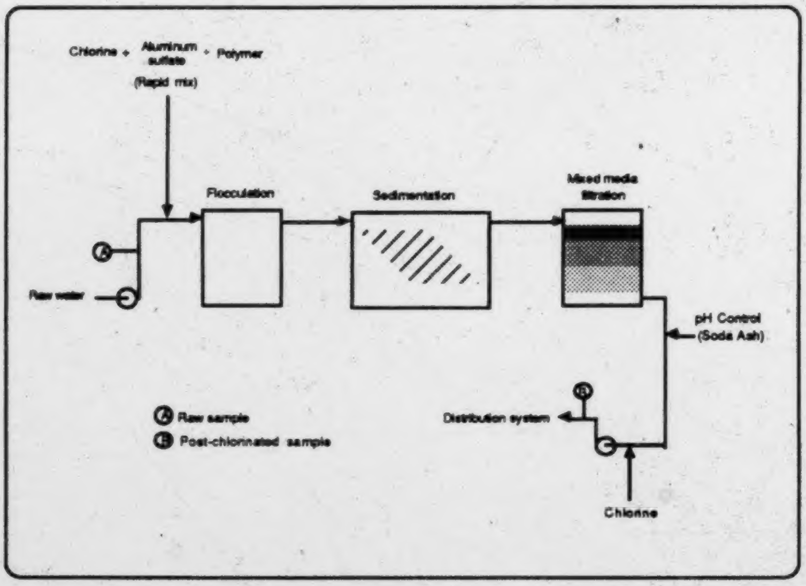

Chlorine + Aluminum sulfate + Polymer
(Rapid mix)
Flocculation
Sedimentation
Mixed media filtration
A
Raw water
pH Control
(Soda Ash)
B
A Raw sample
B Post-chlorinated sample
Distribution system
Chlorine

Figure 6.5 Treatment Plant Schematic - Plant F

6.2.2 Chemical Analyses and MX/EMX Results for Individual Plants

Measurements of chlorine, TOC, TOX, MX and EMX were determined at various stages in the water treatment plants (Table 6.2), except for plant B where only the raw water was sampled. Complete sampling results for each treatment plant are shown in Appendix XII. Presence and removal profiles for MX and EMX are shown in Figures 6.6 and 6.7. The left bar in each pair represents the raw water, while the right bar shows the treated water value. The results for MX and EMX were confirmed by SIM-GC/MS. MX and/or EMX were identified in all extracts of pre-chlorinated raw water (Plants A and C) and in two of four extracts of lab-chlorinated raw water (Plants B and F).

6.2.3 Relationship of MX Concentration to TOC and TOX

6.2.3.1 Raw Water

For pre-chlorinated samples obtained from Plants A and C, the concentration of MX increased with respect to TOC concentration (Figure 6.8). MX was found in lab-chlorinated water from Plant F, but was absent in Plant E which reported both similar TOC and TOX concentrations, suggesting that the production of MX may be dependent upon the type of organic carbon precursors present. Although Plant F did practise chlorination prior to flocculation, it was not possible to obtain a sample which represented the effect of adding only chlorine as this oxidant was added simultaneously with aluminum sulfate and polymer. For this reason, a lab-chlorinated

Table 6.2 Treatment Plant Survey MX and EMX Results

Sample Location and Date	pH	Chlorine (a) Total (mg/L)	TOC (mg/L)	TOX (µg/L)	MX (ng/L)	EMX (ng/L)
Plant A (Dec. 21/88)						
Pre-Chlorinated Raw	8.08	0.3	4.9	NA	60	LD
Post-Chlorinated Finished Water	7.70	NA	NA	NA	NA	NA
Plant A (Jan. 24/89)						
Pre-Chlorinated Raw	7.62	0.9	4.2	428	LD	210
Post-Chlorinated Finished Water	7.32	1.0	3.5	NA	LD	648
Plant B (Dec. 16/88)						
Raw (As Received)	7.86	NA	2.7	NA	6	LD
Raw (Lab. Chlorinated)	NA	2.2	2.7	NA	LD	11.6
Plant C (Jan. 09/89)						
Pre-Chlorinated Raw	7.66	0.2	15.9	352	83	LD
Post-Chlorinated Finished Water	6.97	4.3	4.3	607	LD	LD
Plant C (Jan. 23/89)						
Pre-Chlorinated Raw	7.35	1.0	13.5	217	38	31.0
Plant D (Jan. 12/89)						
Raw	7.98	LD	17.0	60	NA	NA
Raw (Lab. Chlorinated)	NA	2.9	17.0	3180	LD	LD
Post-Chlorinated Finished Water	6.11	1.3	21.9 (b)	754	LD	LD
Plant E (Jan. 16/89)						
Raw	7.61	0.3	27.1	145	NA	NA
Raw (Lab. Chlorinated)	NA	16.4	27.1	3750	LD	LD
Post-Chloraminated Finished Water	7.52	NA	5.4	245	LD	LD
Plant F (Jan. 19/89)						
Raw	7.64	LD	24.1	307	NA	NA
Raw (Lab. Chlorinated)	NA	8.4	24.1	3360	60	0.8
Post-Chlorinated Finished Water	7.58	2.4	8.2	1010	27	38.9

LD=Less than detection limit of : MX 2 ng/L; EMX 0.5 ng/L

NA=Sample not analyzed

(a) Chlorine concentration of pre-chlorinated raw and post-chlorinated finished water measured immediately following sample collection, chlorine concentration of lab-chlorinated samples measured following 40 to 60 hour reaction time

(b) Result confirmed by repeat analysis

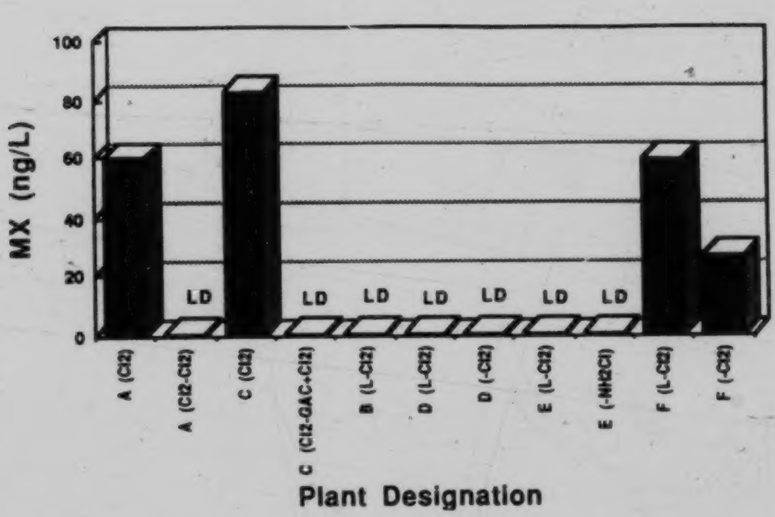


Figure 6.6 Treatment Plant survey: Presence and Removal of MX

Cl_2: pre-chlorination; Cl_2-Cl_2: pre-chlorination and post-chlorination;
Cl_2-(GAC)-Cl_2: pre-chlorination, GAC prior to post-chlorination;
L-Cl_2: laboratory-chlorination; -Cl_2: post-chlorination only;
-$NHCl_2$: post-chloramination only; LD: less than detection limit of: MX 2 ng/L, EMX 0.5 ng/L

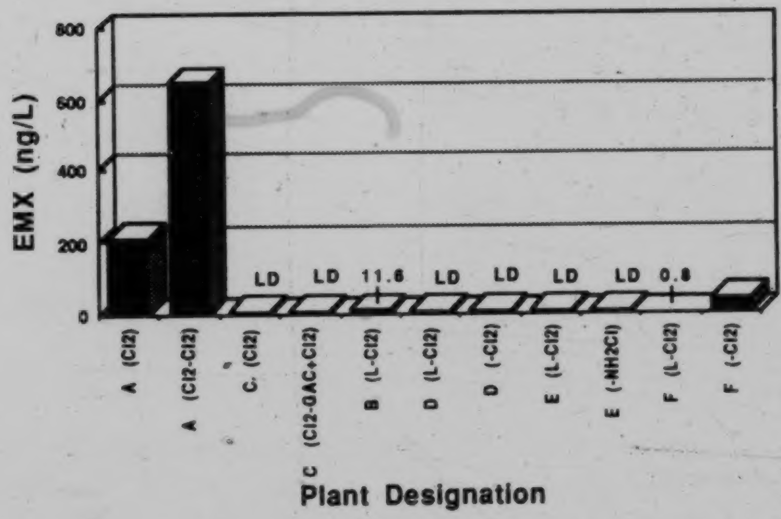


Figure 6.7 Treatment Plant Survey: Presence and Removal of EMX

Cl_2: pre-chlorination; Cl_2-Cl_2: pre-chlorination and post-chlorination;
Cl_2-(GAC)-Cl_2: pre-chlorination, GAC prior to post-chlorination;
L-Cl_2: laboratory-chlorination; -Cl_2: post-chlorination only;
-$NHCl_2$: post-chloramination only; LD: less than detection limit of: MX 2 ng/L, EMX 0.5 ng/L

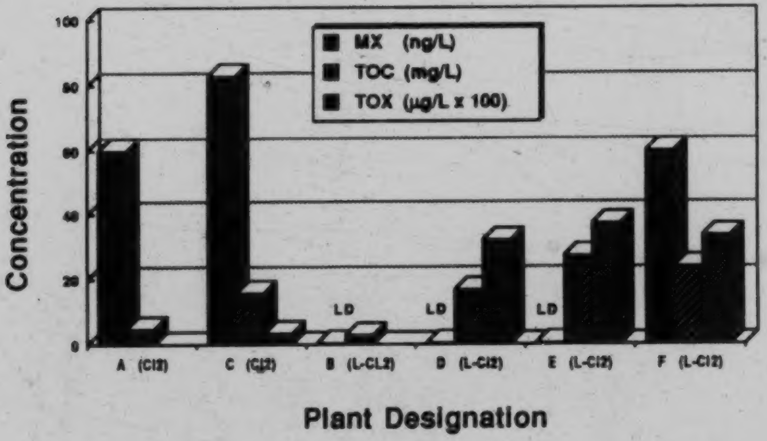


Figure 6.8 Raw Water Results for Selected Water Treatment Plants

Cl_2: pre-chlorination
L-Cl2: laboratory-Chlorination
LD: less than detection limit of: MX 2 ng/L, EMX 0.5 ng/L

sample was prepared which allowed comparisons to be made with other plants. MX was absent in lab-chlorinated raw water from Plants B and D, both of which experienced lower TOC levels. Although specific precursors for MX have not been identified these results suggest that to minimize formation of MX, prechlorination of raw water which is high in TOC should be avoided.

6.2.3.2 Finished Water

Of the five plants where finished water samples were analyzed, MX was detected only at Plant F, at a concentration of 27 ng/L (Table 6.2 and Figure 6.9). Figure 6.10 compares lab-chlorinated water to post-chlorinated finished water for this plant. This figure provides only a qualitative comparison because the chlorine dosage was much higher in the laboratory experiment, due to the higher TOC, and the contact time was considerably longer. However, the figure indicates a good general correlation among TOC, TOX, and MX, and suggests that MX precursors may be removed during treatment. The high TOX values for the unchlorinated raw water in Plants D, E, and F were attributed to difficulties with the nitrate wash step (which removes chlorides) for these turbid samples. The lab-chlorinated TOX values for these samples may have also been high for this reason. However, the data were considered valid as a relative indication of chlorinated by-product formation. MX was noticeably absent in both Plants A and C finished waters (Table 6.2 and Figure 6.9). Although the post-chlorination residual was quite high (4.3 mg/L) at plant C, this plant incorporates GAC as a final treatment step prior to post-chlorination. It would appear that MX

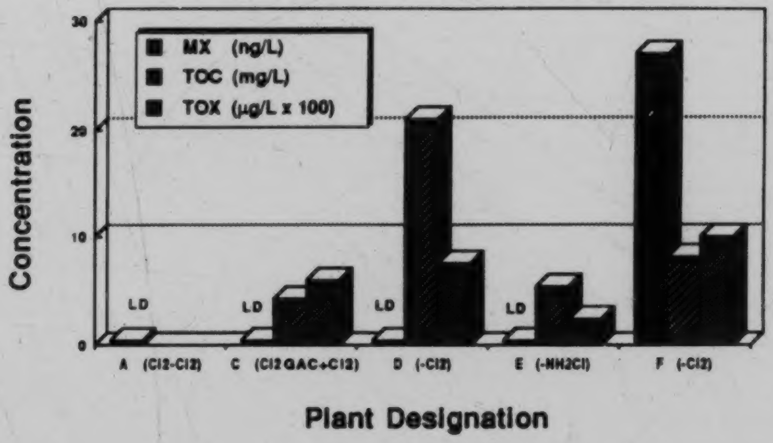


Figure 6.9 Finished Water Results for Selected Water Treatment Plants

Cl2-Cl2: pre-chlorination and post-chlorination
Cl2-(GAC)-Cl2: pre-chlorination, GAC prior to post-chlorination
-Cl2: post-chlorination only; -NH2Cl: post-chloramination only
LD: less than detection limit of: MX 2 ng/L, EMX 0.5 ng/L

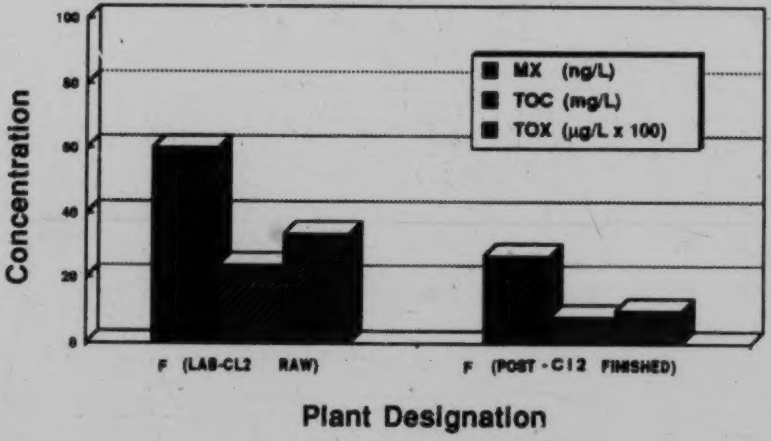


Figure 6.10 Comparison of Laboratory-Chlorinated Raw Water and Post-Chlorinated Finished Water for Plant F

precursors were removed by the GAC.

6.2.4 Results for EMX

EMX was detected in both pre-chlorinated and post-chlorinated plant samples, and in lab-chlorinated water (Table 6.2). The correlation with MX was not consistent. In some cases EMX was present when MX was not (e.g. Plant A, January 24), while in other instances both MX and EMX were detected (e.g. Plant C, January 23). Obviously the factors affecting the relative concentrations of MX and EMX following chlorination require further study.

6.3 Analysis of Solvent Extracts and GAC for MX

6.3.1 Analysis of Solvent Extracts from Previous Studies

Portions of XAD-2 extracts of water sampled in October 1986 and April 1987 from the chlorine stream of a pilot scale water treatment plant located in Edmonton, Alberta were derivatized and analyzed by GC/ECD and GC/MS for the presence of MX and its associated compounds. None were found. This was not unexpected because the water's organic matrix was concentrated on the XAD-2 resin at neutral pH and it is known that these are poor conditions for adsorption of acidic compounds such as MX (Daignault et al., 1988). As well, the samples had been stored for several months (4°C in the dark) before derivatization. During this time MX degradation may have occurred.

6.3.2 GC/MS Analyses of GAC Extracts From Previous Studies

In July 1988, two GAC samples collected from water treatment plants and one sample from a pilot plant which used chlorination were analyzed for the presence of MX. These samples were intended only to serve as a pre-screening tool. If MX was found in the carbon extracts then a more comprehensive evaluation of MX formation and removal in the treatment process could be designed if required.

The two initial samples which were analyzed had been obtained approximately six months earlier and stored at 4°C in the dark prior to analyses. Since it was very likely that some MX degradation may have occurred in these samples a third sample obtained from a large pilot scale study was analyzed within a week of the time of collection. Results for these samples are discussed in the following two sections.

6.3.2.1 Aged Carbon

GAC obtained from the full scale carbon beds of Plant A and from the chlorine stream carbon contactor of the pilot plant mentioned in Section 6.3.1 were Soxhlet extracted for 24 hr with a 50:50 mixture (v/v) of dichloromethane and methanol as recommended by Jackson et al. (1987). Extracts using acetone and ethyl acetate were also obtained to compare extraction efficiencies for future experiments. These were all derivatized and analyzed by GC/ECD for MX and its associated compounds. Small peaks were observed in the chromatograms of the samples at approximately the same relative retention time as that for MX, however, subsequent GC/MS analysis of the extracts showed these peaks were not MX. Compounds normally associated with MX (e.g. EMX) similarly were not observed.

Total ion current chromatograms for these samples are shown in Figures XIII.1a and XIII.1b in Appendix XIII. Trichlorophenol was the only halogenated compound identified in the pilot plant GAC extract. Ethylmethyl-1H-pyrrole-2,5-dione isomers were tentatively identified for two peaks, with good mass spectral matches to library data (scans 260 and 264). All other identified compounds were methyl esters of aryl or alkyl acids, alkyl benzenes or alkyl naphthalenes.

No halogenated products were recovered from the Plant A extracts. Compounds identified in this sample were similar to those identified in the pilot plant extracts.

GC/MS analyses were not performed on GAC extracts using other solvents because the above results using dichloromethane and methanol indicated that MX was not present.

6.3.2.2 Fresh Carbon

Filtrasorb 300® GAC was used in a pilot scale column which was operated in parallel with larger GAC contactors at Plant A for approximately 60 days (7500 bed volumes) during April and May 1989. A sample of the carbon was collected 0.6 m from the top of the column and shipped to the University of Alberta for analysis.

Approximately 50 mL of the GAC was centrifuged to remove excess moisture and Soxhlet extracted with ethyl acetate for 24 hours. The extract was then derivatized and analyzed by GC/ECD and GC/MS. Figure XIII.2 (Appendix XIII) shows the total ion current chromatogram from the GC/MS analysis. A small peak in both chromatograms had approximately the same relative retention time as that expected for MX. Analysis of the mass spectra at and near that peak, however, indicated that MX was not present. The only halogenated compound tentatively identified in this sample was trichloroacetic acid (scan 156).

6.3.3 GC/MS Analyses of GAC Obtained During Treatment Plant Sampling

The purpose of attempting to recover MX and EMX from carbon was to show that removal of these compounds by activated carbon was at least partly attributable to adsorption, and not an attempt to establish a quantitative mass balance. Low recoveries were expected on the basis of desorption work to be described in Section 6.5.

Both MX and EMX were identified in the dichloromethane extract of GAC obtained from Plant A (Table 6.3). (The GAC contactors had been taken off line and were not in use when treated water samples were obtained on December 21 and January 24 from this plant.) The fact that the MX and EMX originated in the water treatment plant and were not either originally present on the GAC or artifacts of the extraction/derivatization procedure was confirmed by analysis both of underivatized extract and of derivatized extract of virgin GAC. The extract of GAC from Plant C showed less than detectable levels of MX or EMX.

Table 6.3 Treatment Plant Survey GAC Extraction Results

Sample Location and Date	MX (ng/g)	EMX (ng/g)
Plant A (Dec. 21/88)		
GAC Extract	114	224
Plant C (Jan. 09/89)		
GAC Extract	LD	LD

LD=Less than detection limit of: MX 1.5 ng/g; EMX 0.4 ng/g

6.4 Quantitation of MX Removal by GAC

6.4.1 Preliminary Investigations

6.4.1.1 Decomposition Investigations

Prior to conducting isotherm experiments, two experiments were performed to measure the decomposition of MX in water at drinking water pH values. In the first experiment, samples were prepared containing approximately 5 µg/L of MX. The Milli-Q® water containing MX was buffered to a pH of 6.5 and was allowed to equilibrate for 30 minutes prior to loading into glass sample bottles. The samples were then placed in a rotary tumbler (at 20°C) and removed at time intervals of 0, 1, 2, and 3 days. Results are summarized in Table 6.4. The time to a 50% reduction in water at pH 6.5 and 20°C was determined to be approximately 1.5 days. These results agree with the observations of Meier et al. (1987) in which MX stability was deduced by measuring the change in mutagenic activity rather than by measuring MX concentrations directly.

In an effort to reduce the loss of MX over time for subsequent isotherm experiments, a second experiment monitoring MX decomposition was designed with some modifications: the pH was reduced from 6.5 to 6.0, and the initial MX concentration in solution was increased from 5 µg/L to 20 µg/L. Under these conditions, a 50% reduction was observed folowing approximately 2.3 (Table 6.4 and Figure 6.11).

6.4.1.2 Isotherm Investigations

On the basis of the decomposition experiments, a preliminary

Table 6.4 MX Decomposition in Pure Water

Experiment 1 (pH=6.5)

Time Days	MX* µg/L	Percentage Recovery+ %
0	5.4	100
1	3.7	67
2	2.0	36
3	2.5	46
21	0.2	4

Experiment 2 (pH=6.0)

Time Days	MX* µg/L	Percentage Recovery+ %
0	20	100
2	13.6	68
2.5	6.8	34
3.0	8.5	43
3.0	239	146±
3.0	6.4	32

* GC analysis performed with SPB-1 column

+ Based on initial MX concentration at time zero

± This value is inconsistent with others-reason is unknown

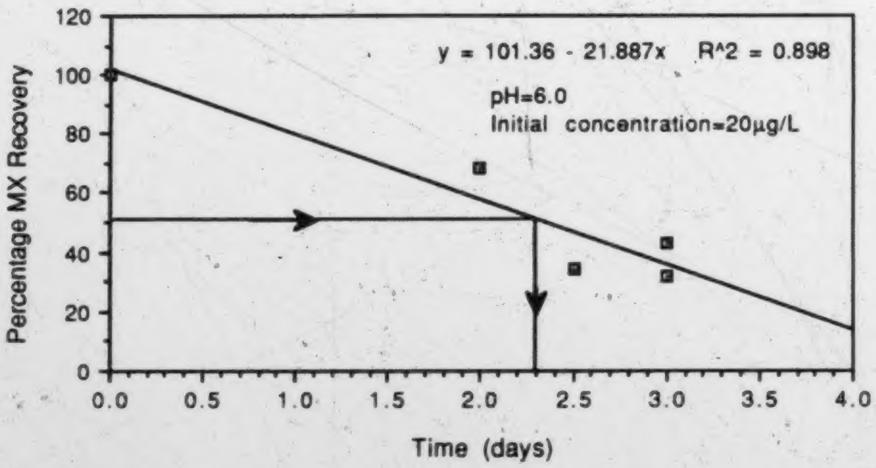


Figure 6.11 MX Decomposition Kinetics

isotherm experiment was designed using an initial MX concentration in water of 30 μg/L, an equilibration time of 2.5 days, a pH of 6.0 and a temperature of 20°C. These conditions were chosen to maximize the number of bottles with detectable concentrations of MX remaining in solution at the end of the experiment while conserving the limited amount of MX available. The other alternative, decreasing the carbon doses, was not feasible because preliminary estimates had shown that very low doses were already required.

The concentration of MX remaining in bottles without activated carbon following a 2.5 day equilibration time was 21.7 μg/L (average of 5 samples). In order to take MX degradation in solution into account, this served as the initial liquid phase concentration (C_{io}) in the calculation of the activated carbon surface loading (q_i). The Freundlich K parameter (representing the adsorptive capacity of the carbon at a given equilibrium concentration) was calculated to be 11,900 μg/g and 1/n (effect of concentration on capacity as represented by slope) was 0.26. For simplicity the units of K are abbreviated as μg/g instead of $(\mu g/g)(L/\mu g)^{1/n}$. These values are typical of a compound which is very well adsorbed and has a very favourable isotherm (i.e. loading is not a strong function of concentration). However, in the case of MX, removal by activated carbon may involve reaction on the carbon surface in addition to adsorption.

In order to confirm the calculated K and 1/n values and expand the range of equilibrium concentrations tested, a second isotherm experiment was designed. The initial MX concentration was increased from 30 to a nominal value of 60 µg/L in an attempt to provide detectable equilibrium concentrations at higher carbon dosages. The initial MX mixing time prior to filling isotherm bottles was increased from 60 minutes to 120 minutes in an effort to ensure that a uniform distribution of MX in the vessel was obtained. All other conditions remained unchanged from the previous experiment.

Figure 6.12 summarizes the results. Good confirmation of the preliminary results was obtained with K and 1/n values of 12,400 µg/g and 0.21, respectively being determined.

The results summarized in this section are discussed in more detail by Huck et al. (1988) and Andrews et al. (1988).

6.4.2 Isotherms with Pre-Loaded Filtrasorb 400®

The reduction in GAC capacity attributable to adsorbed background organics can be very significant in practice (e.g. capacity in lower segments of full scale beds may be reduced by 70 to 80% (Huck and Andrews, 1988). To assess this effect for MX, isotherm experiments were conducted using carbon which had been "pre-loaded" for a period of 10 weeks. The procedure used to obtain the pre-loaded carbon was described in detail in Chapter 4, Materials and Methods. Briefly it involved placing a small column (5.0 cm dia.) containing GAC on stream at a location in a water treatment plant where use of GAC might be proposed. For isotherms involving the pre-loaded carbon an initial MX concentration of 60 µg/L was selected and an equilibration period of 2.5 days was used as in previous isotherm experiments involving virgin carbon. This

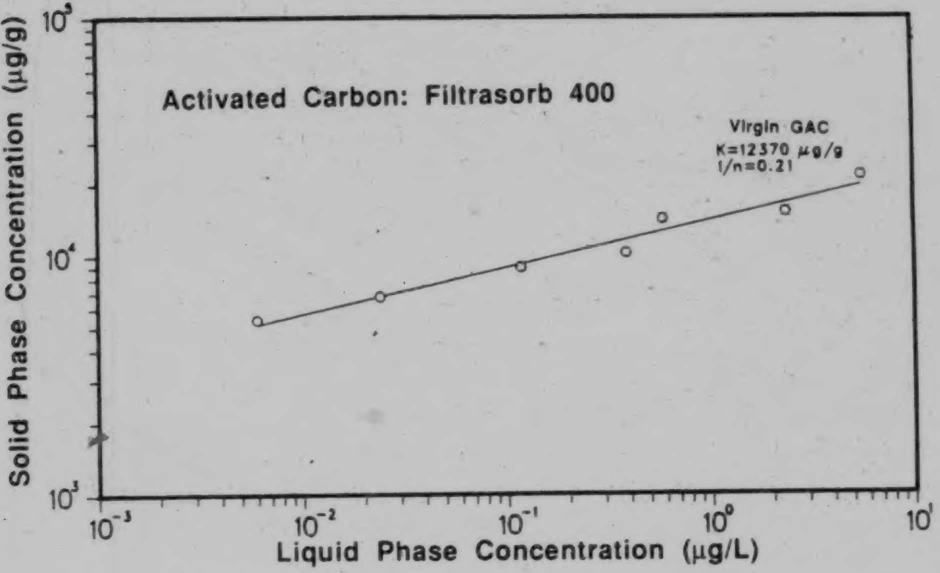


Figure 6.12 MX Single Solute Isotherm (Solid phase concentration assumes that only adsorption and not reaction occurs)

period was chosen despite the fact that slower kinetics were expected when using pre-loaded carbon, because minimization of MX degradation was judged to be more significant than possible non-attainment of equilibrium. Huck and Andrews (1988) have shown that for trihalomethanes, equilibrium using a similar pre-loaded carbon took longer than for virgin carbon, but was 90% attained in less than one day.

Freundlich parameter estimates for pre-loaded carbon are compared to parameters obtained using virgin carbon in Table 6.5. As expected, a capacity reduction for MX attributable to pre-loading was observed by the reduction in K from 12,400 to 4970 µg/g. Confidence intervals (95% CI) for virgin and pre-loaded carbon isotherms did not overlap (Andrews et al., 1988; Huck et al., 1990), indicating that the two isotherms are statistically different (Figure 6.13). On the basis of the Freundlich capacity term K, only 40% of initial capacity remained following 10 weeks of pre-loading. From a practical stand-point, the capacity of activated carbon for MX would be expected to be reduced the most in lower GAC contactor bed depths where pre-loading by background organics is most significant (Andrews, 1987; Baldauf, 1986). The isotherm slope increased from 0.21 to 0.50 indicating that MX removal to low levels would require higher carbon dosages than suggested by virgin carbon isotherms. The shift in slope could also, however, reflect a change in removal mechanism (adsorptive vs reactive) on the pre-loaded carbon due the presence of material that MX could react with.

Table 6.6 compares capacity reduction for MX due to pre-loading for two concentrations which encompass the range defined

Table 6.5 Freundlich Parameters for MX Adsorption on Virgin and Pre-Loaded Carbon

Pre-loading Time, Weeks	Equilibration Time, Days	pH	K(µg/g)(L/µg)^1/n NLLS Fit*	Approximate 95% Confidence Interval**	1/n NLLS Fit*	Approximate 95% Confidence Interval**	Concentration Range (µg/L)
0+	2.5	5.93	12400	11400-13400	0.21	0.16-0.25	0.01-5.54
10++	2.5	5.91	4970	2610-7330	0.5	0.29-0.71	0.015-18.1

K values rounded to 3 significant figures
Equilibration temperature: 20°C
Co = 60 µg/L

*NLLS: Non-linear least squares
**Calculation is based on approximations valid in the region of the optimum parameter estimates.

+Virgin carbon
++Pre-loaded carbon

Table 6.6 MX Capacity Reduction Due to Pre-Loading

Influent Concentration (ng/L)	Capacity (µg/g)		Percentage of Original (virgin) Capacity (%)
	Virgin Carbon	Pre-loaded Carbon	
100	7630	1570	21
10	4700	497	11

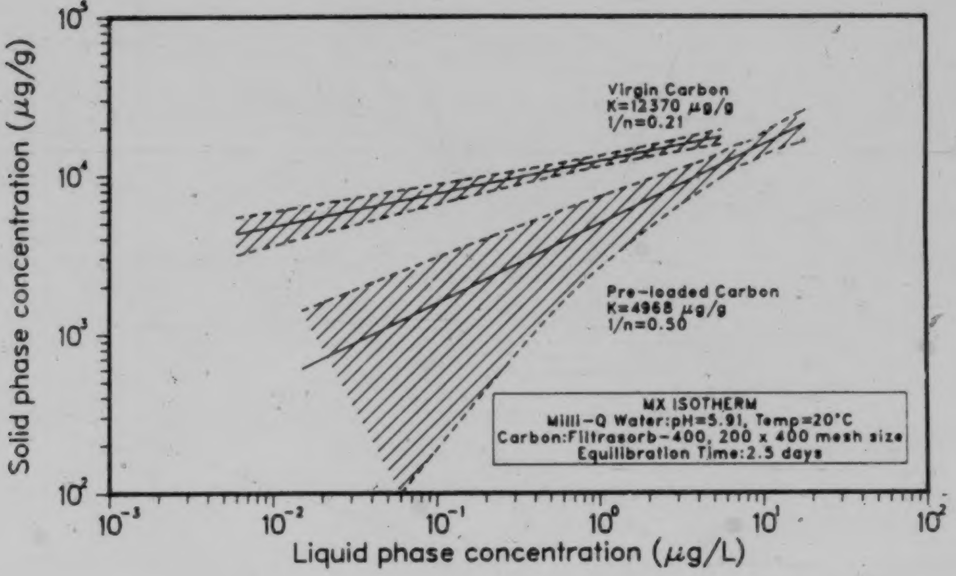


Figure 6.13 MX Single Solute Isotherm-10 Week Pre-Loaded Filtrasorb 400® Showing 95% Confidence Interval (Solid phase concentration assumes that only adsorption and not reaction occurs)

by Kronberg et al. (1988) (10 ng/L to 100 ng/L) expected in conventional water treatment employing the use of chlorine. For the particular water tested, the residual GAC capacity following ten weeks of pre-loading would be approximately 10-20% of the original (virgin carbon) capacity. The effect of pre-loading on capacity reduction became more significant as the concentration to be removed decreased.

6.4.3 Comparison of MX Adsorption to That of Trihalomethanes

To relate the capacity of GAC for MX qualitatively to that of more widely studied compounds a comparison is provided with the chlorination by-product chloroform, normally the major trihalomethane component (Figure 6.14). The data for chloroform were obtained using Filtrasorb 300® carbon (both virgin and following 8 weeks of pre-loading) at the Buffalo Pound Water Treatment Plant in Saskatchewan as described in Chapter 5. The pre-loading conditions differed at Buffalo Pound from those encountered during the pre-loading of the Filtrasorb 400® GAC used in the MX isotherms in that the time was 8 weeks instead of 10, the total organic carbon was higher and largely of algal origin, biological activity was more likely to develop on the carbon, and THMs were unavoidably present in the water used for pre-loading. Figure 6.14 shows that MX was much better removed than chloroform. Pre-loading reduces capacity at higher concentrations to a lesser extent than chloroform as was observed by the smaller isotherm displacement. This would be expected even with identical

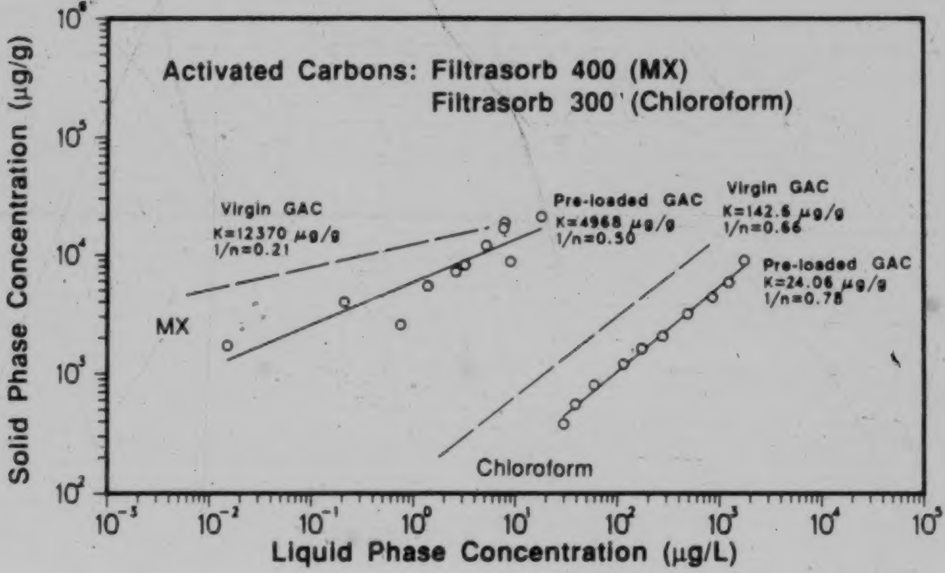


Figure 6.14 Comparison of MX and Chloroform Isotherms (Solid phase concentration assumes that only adsorption and not reaction occurs)

pre-loading conditions because of the higher capacity of activated carbon for MX. For chloroform, capacity was reduced by 83% following 8 weeks of pre-loading whereas only a 60% reduction was noted for MX following 10 weeks of pre-loading. These capacity comparisons were however evaluated at a residual concentration of 1.0 µg/L which is for MX much higher and for chloroform much lower than would be observed following typical drinking water treatment. The data in Figure 6.14 suggest that either pilot or full-scale GAC beds would be exhausted for routinely monitored compounds such as trihalomethanes prior to breakthrough of MX.

6.4.4 Comparison of Virgin Carbon MX Isotherms Conducted at pH 6, 7 and 8

To encompass the finished water pH range normally expected in potable water production, three separate isotherm experiments were conducted at pH 6, 7 and 8. These isotherms were conducted following the adsorption/desorption experiments described in Section 6.5 but are reported here such that all isotherm work would remain in the same section of this chapter.

The experimental procedure was essentially the same as that described in Section 6.4.1.2 except that an initial concentration of nominally 100 µg/L MX was used as opposed to the 30 µg/L or 60 µg/L used previously. This change was initiated in an attempt to obtain a wider residual concentration range. The equilibration time was reduced from 2.5 days to nominally 1 day to reduce the opportunity for MX to be degraded or transformed prior to analysis.

Preliminary isotherms had shown concentration inconsistencies among spiked sample blanks (containing no carbon). The problem was traced to inconsistent MBA area counts. Averaged values of the sample blank concentrations constituted the initial (equilibrated) concentration value (C_{io}) used in isotherm calculations.

A new internal standard, *a*,*a*,2,6-tetrachlorotoluene (TCT) was added in addition to the MBA internal standard used in previous experiments. TCT was selected because it was readily available and had been proven to be a reliable internal standard for aldehyde analysis, which is also a procedure involving derivatization, the samples for which were normally analyzed on the same GC and used similar operating conditions as for MX samples. Unlike MBA, however, the compound TCT was unaffected by derivatization and could be detected by GC/ECD in its natural state.

Complete data for the three isotherm experiments are shown in Appendix XIV. Concentrations for MX were calculated on the basis of both internal standards but were plotted in isotherm form using only the TCT internal standard, which provided greatly improved reproducibility between individual GC analyses for replicate sample injections (e.g. Table XIV.1, Appendix XIV).

Isotherms obtained for Milli-Q® water buffered to pH 6, 7 and 8 are shown in Figures 6.15, 6.16 and 6.17, respectively. Freundlich parameters are reported in Table 6.7. The parameters obtained for pH 6.0 cannot be directly compared with those reported earlier since the equilibration time, initial concentration and internal standard differed.

As pH increases, the adsorptive capacity appears to decrease,

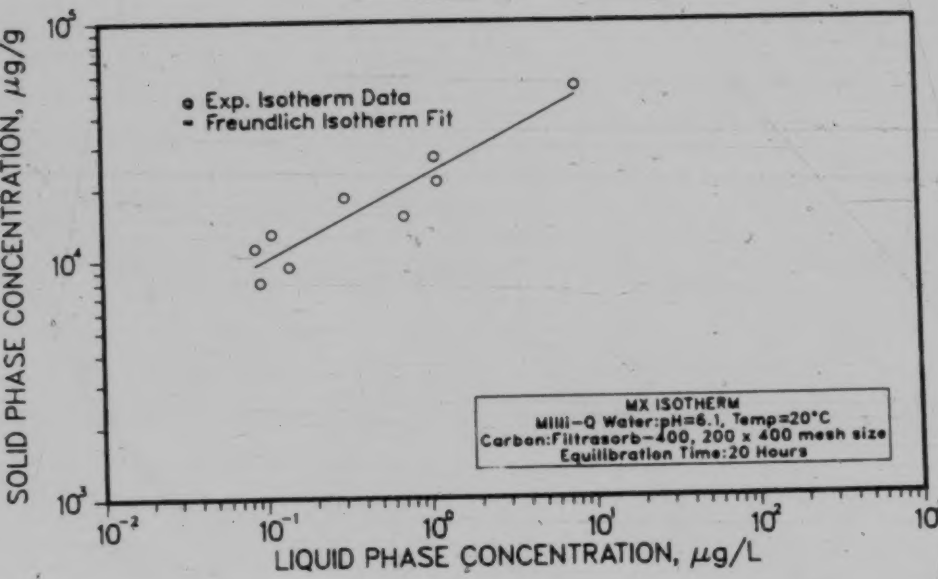


Figure 6.15 MX Single Solute Isotherm (pH 6.0) Obtained Using TCT Internal Standard (Solid phase concentration assumes that only adsorption and not reaction occurs)

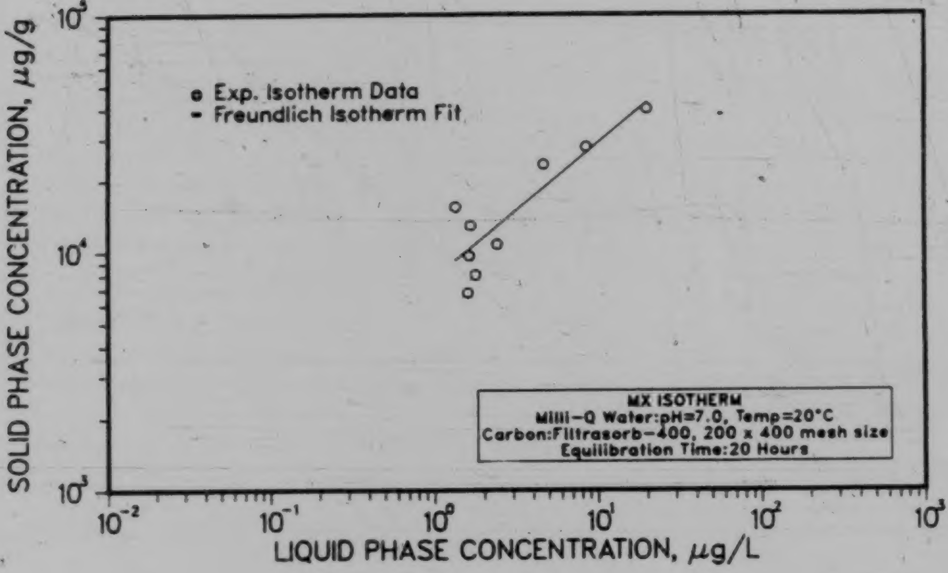


Figure 6.16 MX Single Solute Isotherm (pH 7.0) Obtained Using TCT Internal Standard (Solid phase concentration assumes that only adsorption and not reaction occurs)

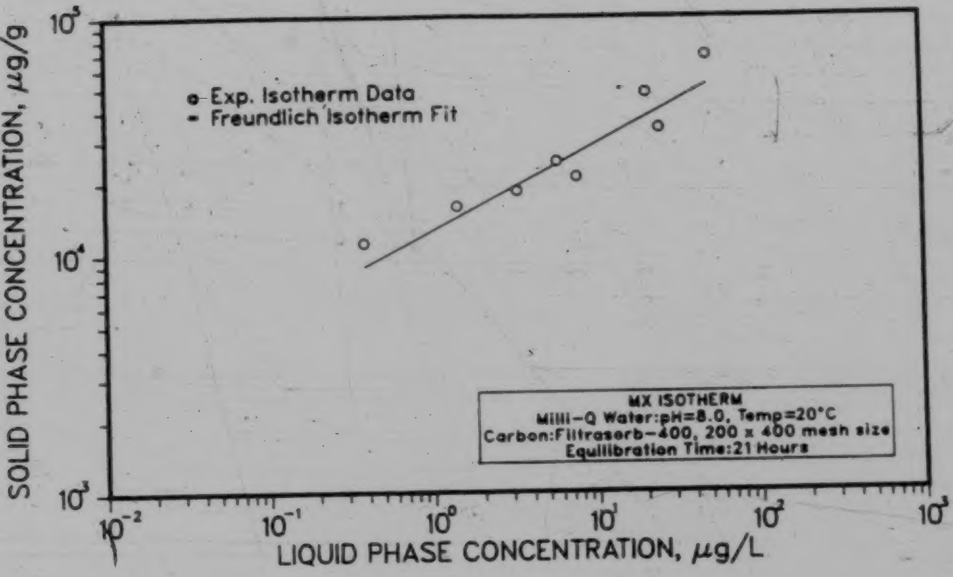


Figure 6.17 MX Single Solute Isotherm (pH 8.0) Obtained Using TCT Internal Standard (Solid phase concentration assumes that only adsorption and not reaction occurs)

Table 6.7 Freundlich Parameters for MX Adsorption on Virgin Carbon at pH 6, 7, and 8

pH	K(μg/g)(L/μg)^1/n NLLS Fit*	Approximate 95% Confidence Interval**	1/n NLLS Fit*	Approximate 95% Confidence Interval**	Concentration Range (μg/L)
6	23200	20600-25800	0.39	0.32-0.45	0.093-8.09
7	8650	6090-11200	0.52	0.39-0.64	1.34-19.8
8	9030	4590-13500	0.5	0.35-0.65	0.38-49.3

Note: All data calculated using TCT internal standard
Co = 100 μg/L
K values rounded to 3 significant figures
Equilibration temperature: 20°C
*NLLS: Non-linear least squares
**Calculation based on approximations valid in region of optimum parameter estimates.

however the confidence intervals for both pH 7 and pH 8 isotherms overlap and therefore the capacities reported cannot be statistically distinguished. The inverse effect of pH on adsorption of MX is consistent with findings of Weber (1972) for organic pollutants. When pH decreases, neutralization of negative surface charges may result because of the increasing hydrogen ion concentration. As a result, more of the active surface of the carbon will be made available at the lower pH values.

Despite the apparent reduction in capacity with increasing pH, MX should be readily removed by activated carbon over the range of pH typically encountered in water treatment practise.

6.4.5 Equilibrium Column Model Predictions

The equilibrium column model (ECM) as previously described in Chapter 5 allows fixed bed column breakthrough to be predicted for individual adsorbates, under the assumption that no mass transfer resistance occurs. Using as input, isotherm parameters determined for MX on Filtrasorb 300® carbon, the ECM was used to predict the number of bed volumes fed to breakthrough for two pH conditions and one pre-loading condition. Results were then compared to the breakthrough of chloroform, a routinely-monitored chlorination by-product.

6.4.5.1 Comparison of MX Breakthrough for Two pH Conditions

The hypothetical breakthrough of MX in a bed containing Filtrasorb 400® carbon was predicted using the ECM for two (pH 6, pH 7) of the three pH conditions reported in Section 6.4.4. No breakthrough predictions are reported for pH 8 as the IAST subroutine in the ECM failed to converge for those input parameters.

The flowrate selected for use in the set of input parameters to the model (12.8 m/hr) was the same as used at the Buffalo Pound water treatment plant during the summer of 1987. As such, this represented an actual operating condition and thereby allowed predictions to be generated for a simulated real life scenario. The physical parameters of both porosity and bulk density were obtained for Filtrasorb 400® carbon from the manufacturer (Calgon Carbon). Hypothetical components (HC's) previously determined for Filtrasorb 300®, representing competition attributable to co-adsorption of background organics were applied in all ECM predictions. The HC approximation for Filtrasorb 400®, however, would introduce only a small error if any, as very little difference was noted between the HC's determined in Chapter 5 for two different carbons (Filtrasorb 300® and Ceca 830®).

The ECM predicted breakthrough profiles for Filtrasorb 400® carbon evaluated at pH 6 and 7 are shown in Figure 6.18. Breakthrough profiles, occurring at 120,000 bed volumes, were identical for both pH values. This result was not unexpected as the Freundlich adsorption capacity for MX is very high at either pH value when compared to other organic compounds such as trihalomethanes, which compete for adsorption sites.

The chosen influent concentration for MX of 0.1 µg/L represented the high end of the range for this compound in cases where it has been found to be present in drinking water treatment.

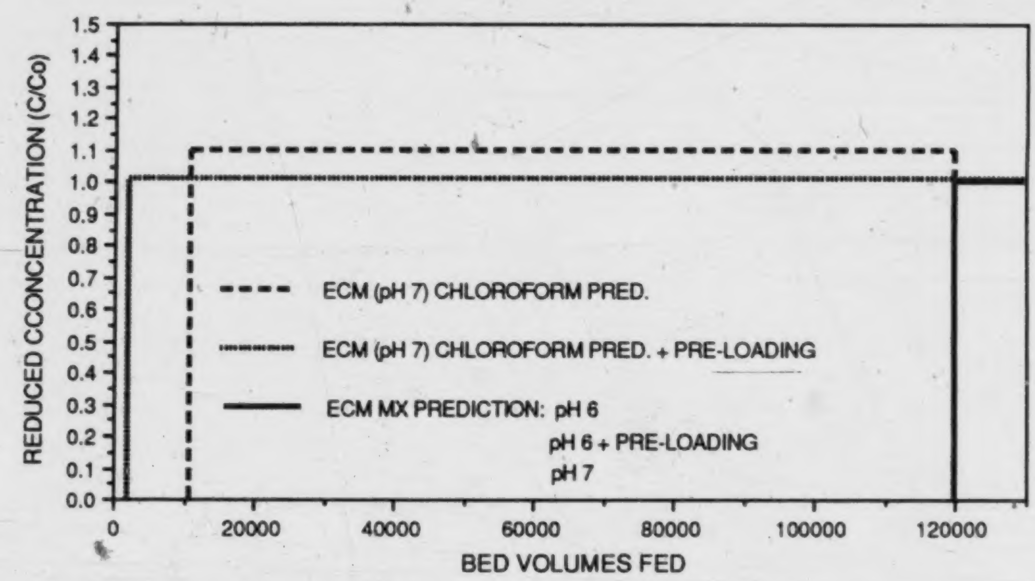


Figure 6.18 ECM Breakthrough Predictions for Chloroform and MX (Filtrasorb 400®)

This value however is at least one to two orders of magnitude lower than the concentration expected for other chlorinated organics such as trihalomethanes. Therefore, since MX was known to be adsorbed very well and was present only in small quantities, a large value for bed volumes fed to breakthrough was anticipated.

Breakthrough was also predicted at pH 6 for isotherm parameters obtained using carbon which had been pre-loaded with background organics for a period of 10 weeks. A complete discussion of actual pre-loading conditions was presented in Section 6.4.3. Despite a capacity reduction of approximately 60%, the values of bed volumes fed to breakthrough as predicted using the ECM did not change (Figure 6.18) due to the high adsorbability and low influent concentration discussed earlier.

6.4.5.2 Comparison of ECM Predictions for MX and Chloroform

The effect of capacity reduction due to pre-loading was directly compared for MX and chloroform at pH 7 using the ECM. This prediction comparison was conducted to confirm isotherm capacity estimates presented in Section 6.4.3 which suggested that despite capacity reductions due to pre-loading, breakthrough of MX in carbon adsorbers would occur much later than routinely monitored compounds such as trihalomethanes.

For comparison purposes, a pH of 7 was selected since isotherm experiments for chloroform using pre-loaded carbon were previously conducted at this value.

Assuming that no change in ECM predicted bed volumes fed to breakthrough would occur for MX at pH 7 when compared to pH 8 (as was the case for pH 6) a direct comparison is shown between breakthrough of chloroform and MX in Figure 6.18. Using a typical contactor operating flowrate and chloroform influent concentration, and assuming a relatively high influent concentration for MX (0.1 µg/L), breakthrough for chloroform would occur approximately 11 to 64 times earlier than for MX, depending on pre-loading conditions. The values for chloroform breakthrough shown in Figure 6.18 were predicted for both virgin carbon and carbon pre-loaded for approximately 10 weeks as described for MX. Thus, a maximum range of breakthrough values for chloroform were obtained.

6.5 Adsorption/Desorption Investigations

6.5.1 Introduction

While the isotherm data presented in Sections 6.4.1.2 to 6.4.4 appear to follow an adsorption mechanism as described by the Freundlich equation, the ultimate goal of applying predictive modelling to the removal of mutagenic compounds such as MX and EMX from water requires that the removal mechanisms be known. Work described in this section was performed in an attempt to elucidate whether the removal mechanisms are based on physical adsorption or chemical reaction. Since MX reacts in water, it may also react on the surface on carbon to form other compounds. To evaluate the adsorption hypothesis, and to some extent determine if reaction occurs, attempts were made to desorb MX, EMX and other organics following adsorption on activated carbon. The general procedure for these experiments is described in the following section. Detailed experimental data pertaining to the adsorption/desorption experiments is shown in Appendices XV and XVI.

6.5.2 General Procedures

To initially adsorb MX and EMX onto carbon for subsequent desorption experiments, Milli-Q® water containing known amounts of MX and EMX was adjusted to pH 6.0 with phosphate buffer and measured into 160 mL serum bottles. It was then equilibrated in the same manner as for isotherms. The solute concentration and carbon dosages to achieve target loadings were calculated using the Freundlich equation and parameters determined from single solute isotherms. Carbon blanks (solutes only, no carbon) were prepared and equilibrated with the above solutions to account for the natural degradation of MX and EMX in water at pH 6.0. At least one Milli-Q® water blank, containing no MX or EMX, was also included. Standards were prepared in ethyl acetate to include both the high concentrations expected in the water blanks and the low concentrations expected in the supernatant extracts.

After equilibration, bottles containing carbon were centrifuged to enhance settling of the carbon and 150 mL of the supernatant solution was removed. As described in the Methods section, the supernatant was extracted with three portions of ethyl acetate (EtOAc) which were combined, dried with sodium sulfate crystal, derivatized and then analyzed by GC/ECD to determine the equilibrium liquid phase concentrations of MX and EMX. In some experiments acetone, 7% methanol in dichloromethane (MeOH:DCM) or 50% MeOH:DCM were also used in place of ethyl acetate, depending on the type of solvent system to be used in a subsequent desorption step.

As much as possible of the liquid, which remained in the bottles containing carbon, was removed with Pasteur pipets and the volume recorded. After the remaining liquid was acidified to pH ≤ 2 with 2M sulfuric acid, 150 mL of organic solvent was added and the bottles were allowed to re-equilibrate (desorb) for 1 day. Acidification was used in this step to prevent further degradation of MX and to permit more efficent extraction of MX (pK_a=5.25) into the organic phase.

Soxhlet extraction was considered but could not be employed to desorb solutes from the carbon due to the inability of Soxhlet thimbles to retain small carbon particles. Following re-equilibration, the solvent layer was separated from the aqueous layer and remaining carbon either by using separatory funnels fitted with small glass wool plugs or by directly pipetting aliquots of the organic layer into a round bottom flask. The solvent layer was dried over sodium sulfate crystal, reduced in volume using rotary evaporation, derivatized and then analyzed by GC/ECD to determine the amount of solute desorbed from the carbon. In some experiments a displacer (benz[a]anthracene or benz[a]anthracene-7,12-dione) was added to the solvent in an attempt to improve recovery of MX and EMX. In these cases the sample handling procedure was exactly the same as with solvent alone.

For most experiments, the general procedure described above was utilized as written. However, initial studies involved two desorption steps in which the aqueous layer and carbon from the first desorption was transferred to 500 mL glass bottles with Teflon®-lined screw caps for a second desorption. Ethyl acetate (300 mL) was added to each bottle and the bottles were re-equilibrated for a total of 2.8 days. The carbon was then allowed to settle by gravity before a 250 mL ethyl acetate aliquot was removed, dried, concentrated, derivatized and analyzed by GC/ECD to determine the amount of solute desorbed from the carbon.

In total, six experiments were designed and conducted to evaluate the desorption efficiency of various solvent systems both with and without the presence of a displacer compound. Procedures relevant to each individual experiment and results obtained are presented in separate sections for each experiment. Desorption experiment analyses were performed by C. Laverdure and S. Daignault, Department of Civil Engineering, University of Alberta.

6.5.2.1 Solvent Selection

Four different solvents or mixtures of solvents were evaluated for their potential to desorb MX from carbon. These were:

i) ethyl acetate (± benz[a]anthracene-7,12-dione)
i) acetone (± benz[a]anthracene-7,12-dione)
iii) 7% methanol in dichloromethane (with benz[a]anthracene-7,12-dione)
iv) 50% methanol in dichloromethane (± benz[a]anthracene-7,12-dione)

Ethyl acetate was used because it is the solvent commonly employed to extract MX and EMX from water and is the solvent in which these compounds are most stable (Kronberg et al., 1985). Acetone was used in studies by Ho and Daw (1988) to remove 2,4-dinitrotoluene from Filtrasorb 300® and Filtrasorb 400® activated carbons. A mixture of 50% MeOH:DCM was used by Jackson et al. (1987) to remove chlorination by-products from GAC.

Thakkar and Manes (1987, 1988) found benz[a]anthracene-7,12-dione (1.5 g displacer in 25 mL dichloromethane containing 7.5 vol % methanol) to be effective in completely displacing approximately half of the 25 base-neutral priority pollutants which had been pre-loaded on powdered Filtrasorb 400®. In initial experiments, 0.5 g of benz[a]anthracene was used as the displacer because no benz[a]anthracene-7,12-dione was available at the time. Benz[a]anthracene is known to be less strongly adsorbed than benz[a]anthracene-7,12-dione (Thakkar and Manes, 1987) and therefore was expected to displace less MX.

6.5.2.2 Standard Preparation and GC/ECD Response Calculation

In general, a separate series of standards was prepared for each experiment. Concentrations were selected such that detailed response data for both low and high concentration ranges could be obtained. The low range was used to calculate residual concentrations present in the supernatant following adsorption on activated carbon. The high response range was used to calculate the MX spiking concentrations present in bottles which contained no carbon.

To accomodate the wide concentration range but maintain constant solution volumes (and thus, general physical conditions) during derivatization, typically three to four working standards of varying MX and EMX concentrations, prepared from a single stock solution, were used to prepare the standard solutions to be used for instrument calibration. Volumes of 1.0 to 10.0 µL were used to prepare standards ranging from 0.5 to 1000 ng whereas 10.0 to 40.0 µL were used for standards ranging from 1,000 to 100,000 ng. By using this method, the volume of working standard added to 1.0 mL of EtOAc could be kept within a narrow range and the total standard solution volume could be kept fairly constant over the entire range of concentrations employed. 10 µL of a 0.1305 µg/µL MBA internal standard was added to each standard and, in all cases, derivatization of standards followed the same procedure as for samples.

Typical standard data and corresponding GC/ECD area counts are shown in Appendix XV (Table XV.1 to Table XV.2). Representative MX/MBA mass ratio vs MX/MBA area ratio response curves are also shown in Appendix XV (Figures XV.9 to Figures XV.10). Both MX and EMX response curves exhibited nonlinear responses for area ratio ranges of 0 to 1.0 and 0 to 2.5, respectively. This nonlinearity however was not unexpected. Perry (1981) states that obtaining full accuracy and precision from gas chromatography requires abandoning the assumption that detector response is linear from the origin through the highest concentration. To obtain optimum performance, Perry (1981) suggests calibrating often with known mixtures that closely bracket the component concentration ranges within the sample group.

A method of establishing instrument response described by Harris and Kratochvil (1981) suggests plotting data to observe if curvature is present prior to determining a response equation. Results for three separate experiments were combined to produce the response curve shown in Figure XV.9, Appendix XV illustrating that low end curvature was indeed present.

Possible reasons for the low end MX and EMX response curvature include preferential adsorption of MX and EMX as opposed to MBA onto the glass vials used for standard preparation (Cantwell, 1989) and preferential thermal decomposition in the GC injection port (Williams, 1989).

To produce a line of best fit, Harris and Kratochvil (1981) recommend using a least squares type of analysis. Data for all plots which were deemed linear was subjected to a linear least squares fitting routine. Responses for curvilinear data were subjected to a nonlinear least squares analysis for the determination of individual equation parameters. Response curve fits for both linear and nonlinear cases are shown in Appendix XV (Figures XV.9 to XV.10) along with their corresponding 95% confidence intervals. Application of typical response and confidence interval data resulted, for example, in a 6.8% precision for desorption recovery calculations when MX/MBA area ratios were approximately 1.0.

6.5.2.3 Solute Recovery Calculations

An internal standard, mucobromic acid (MBA), was added to each sample prior to derivatization as described in the Methods section. The area counts obtained from GC/ECD analysis could then be related to a known amount of MBA and thus allow the mass of MX or EMX to be calculated. The following equations illustrate these calculations for MX. Similar calculations would apply to EMX.

Calculation of mass ratio (MX/MBA):

i) in the case of linear EC detector response

$$\left(\frac{\text{mass MX}}{\text{mass MBA}}\right) = \text{y-intercept} + \text{slope} \cdot \left(\frac{\text{area MX}}{\text{area MBA}}\right) \qquad (6\text{-}1)$$

ii) in the case of non-linear EC detector response; quadratic approximation

$$\left(\frac{\text{mass MX}}{\text{mass MBA}}\right) = \text{y-intercept} + a \cdot \left(\frac{\text{area MX}}{\text{area MBA}}\right) + b \cdot \left(\frac{\text{area MX}}{\text{area MBA}}\right)^2 \qquad (6\text{-}2)$$

where: a and b are coefficients determined using non-linear least squares regression analysis

Calculation of mass (MX):

Using mass ratios obtained from Equations 6-1 or 6-2,

$$\text{mass of MX} = \left(\frac{\text{mass MX}}{\text{mass MBA}}\right) \cdot \text{mass MBA} \qquad (6\text{-}3)$$

To express this value as total mass present in for example, a 160 mL serum bottle, the mass obtained from Equation 6-3 was multiplied by the following factor:

$$\text{total mass MX} = \text{mass MX} \cdot \left(\frac{\text{total bottle volume}}{\text{volume extracted}} \right) \tag{6-4}$$

Equations 6-1 to 6-4 would apply to the determination of solute present in (i) a "sample blank" spiked with MX/EMX or (ii) supernatant withdrawn from a bottle containing carbon.

Calculation of net mass of MX recovered from carbon:

A small amount of extraneous water remained with the carbon after the desorption step. To calculate the net amount of MX desorbed from the carbon, the mass of MX present in this small volume of extraneous water (typically 2 to 10 mL) must first be subtracted.

$$\left(\begin{array}{c} \text{net} \\ \text{mass MX} \\ \text{desorbed} \end{array} \right) = \left(\begin{array}{c} \text{total} \\ \text{mass MX} \\ \text{in liquid} \\ \text{phase} \end{array} \right) - \left(\frac{\text{initial mass MX}}{\text{total bottle volume}} \right) \cdot \left(\begin{array}{c} \text{volume} \\ \text{extraneous} \\ \text{water} \end{array} \right) \tag{6-5}$$

The mass of MX present in extraneous water was always low compared to total mass of MX desorbed and was typically less than 5%.

Percentage of MX recovered

The amount of MX recovered was also expressed on a percentage basis using two different methods representing minimum and maximum recoveries, depending on the choice of initial liquid phase concentration. Because of the natural degradation of MX, the actual liquid phase initial concentration (i.e. during the adsorption step) may be assumed for calculation purposes to be either (i) the calculated mass of MX spiked into the buffered water solution or (ii) the mass of MX measured following equilibration of sample blanks which contained no carbon. The second value has typically been used in isotherm mass loading calculations as it accounts for any losses which may occur during equilibration. This was an important consideration for the compound MX which was shown to degrade by approximately 50% following 2.3 days at 20°C in Milli-Q® water at pH 6.0.

(i) Minimum MX Recovery (%)

$$\begin{array}{c}\text{Minimum}\\ \text{MX}\\ \text{Recovered}\end{array} = \left(\frac{\text{mass recovered from carbon}}{\text{initial spiked mass - equilibrated sample mass}} \right) \cdot 100 \qquad (6\text{-}6)$$

The recovery value calculated using Equation 6-6 represents the minimum MX recovery since it does not account for degradation during equilibration. Initial spiked mass (no carbon) and equilibrated sample mass (in the presence of carbon) refer to aqueous phase measurements.

(ii) Maximum MX Recovery (%)

$$\begin{array}{c}\text{Maximum}\\ \text{MX}\\ \text{Recovered}\end{array} = \left(\frac{\text{mass recovered from carbon}}{\text{equilibrated spiked mass - equilibrated sample mass}} \right) \cdot 100\% \qquad (6\text{-}7)$$

Equilibrated spiked mass (no carbon) and equilibrated sample mass (in the presence of carbon) refer to aqueous phase measurements. The recovery value calculated using Equation 6-7 is larger than that calculated by Equation 6-6 as it takes into account the possible lower spiked mass of MX due to degradation which occurs during equilibration. By evaluating recoveries based on both Equations 6-6 and 6-7, an upper and lower bound could be reported.

6.5.3 Desorption Using Ethyl Acetate (Expt. AD-88-1)

6.5.3.1 Procedure

To initially select three different carbon dosages, a computer program previously designed to determine optimal dosages for use in isotherm experiments was applied. The constraints for dosage selection were such that the minimum weight of carbon in a 160 mL serum bottle would be 10 mg and the minimum MX concentration, after adsorption corresponding to the maximum carbon dosage would be 0.02 µg/L.

Milli-Q® water was buffered to pH 6.0 in a glass beaker and then transferred to a stainless steel delivery system which was covered with a floating Teflon® cover. Prior to spiking the water with an MX/EMX solution, one water blank was collected. Two additional 160 mL aliquots were also collected. These were spiked with an MX/EMX standard containing 69% MX and 31% EMX to provide nominal concentrations of 100 ng/L (69 ng/L MX; 31 ng/L EMX) and 500 ng/L (345 ng/L MX; 155 ng/L EMX) by injecting 1.3 µL and 6.5 µL of a 12.25 ng/µL solution respectively into 160 mL serum bottles.

These "dilute" water blanks, represented as samples 11 and 12 in Table 6.8, were prepared such that recoveries could be examined in the range of solute concentrations expected in the supernatant following equilibration of bottles containing carbon. At this point in the experiment all three serum bottles were capped with Teflon®-lined butyl rubber septa and aluminum crimp seals.

The remaining volume of water (1520 mL) was spiked with 310 µL of a 4.9 µg/µL solution of MX/EMX to provide a total concentration of 1000 µg/L (690 µg/L MX; 310 µg/L EMX). The solution was then allowed to mix for one hour to ensure uniformity prior to the collection of any further samples. During the bottle filling operation, samples were collected from the delivery system via a needle valve located near the bottom. The solution was stirred using a Teflon®-coated magnetic stir bar throughout the collection of samples.

Carbon blanks (samples which did not contain carbon), designated as 1B, 5B and 9B, as well as samples containing carbon were then filled in the numerical order shown in Table 6.8. These blanks were prepared to account for the natural degradation of MX and EMX in water at the chosen pH. All remaining bottles were then capped with Teflon®-lined butyl rubber septa and aluminum crimp seals as previously described. In total twelve samples were then placed in the tumbler to equilibrate for nominally 1.0 day at 20°C.

Once equilibration was complete, the six samples containing carbon were centrifuged (Sorval/RC 50 centrifuge) for 30 minutes at 1500 rpm to enhance separation of the powdered carbon from the liquid phase. Bottles not containing carbon were excluded from the

Table 6.8 Adsorption Results-Liquid Phase Concentration (Expt. AD-88-1)

Sample Designation	MX Avg. (a) (µg)	EMX Avg.(a) (µg)
1B H2O Ext. (Spiked, no carbon)	57.9	14.2
2 H2O Ext. (Spiked, incl. carbon)	0.047	0.021
3 H2O Ext. (Spiked, incl. carbon)	0.059	0.020
4 H2O Ext. (Spiked, incl. carbon)	0.010	0.020
5B H2O Ext. (Spiked, no carbon)	58.1	8.40
6 H2O Ext. (Spiked, incl. carbon)	0.027	0.020
7 H2O Ext. (Spiked, incl. carbon)	0.006	0.019
8 H2O Ext. (Spiked, incl. carbon)	0.010	0.021
9B H2O Ext. (Spiked, no carbon)	45.5	8.04
10B H2O Ext. (Water only, no carbon)	0.005	0.019
11B H2O Ext. (Spiked 100 ng/L) (b)	0.009	0.019
12B H2O Ext. (Spiked 500 ng/L) (c)	0.024	0.019

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.
(b) Spiked with 100 ng/L MX+EMX; (11.0 ng MX, 5.00 ng EMX in 160 mL)
(c) Spiked with 500 ng/L MX+EMX; (55.2 ng MX, 24.8 ng EMX in 160 mL)

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-13.5 mg, #3-12.4 mg, #4-19.1 mg, #6-19.2 mg, #7-29.6 mg, #8-29.7 mg.

Spike contained MX: 69.0%
EMX: 31.0%

centrifugation. Aliquots of 150 mL were removed from each bottle using a volumetric pipet and filtered to remove any remaining carbon fines into 2 L separatory funnels using funnels equipped with glass wool plugs. The combined extracts were then acidified using 2 M sulfuric acid to pH ≤ 2 and extracted using three portions (37 mL, 22 mL and 22 mL) of double distilled ethyl acetate. All three organic extract aliquots were then combined and once again filtered through a glass wool plugged separatory funnel to remove any remaining carbon fines. The combined extracts were then passed through glass wool plugged separatory funnels containing anhydrous sodium sulfate to remove residual water. They were then concentrated using rotary evaporation to approximately 2 mL and transferred to 40 mL vials using approximately 10 mL of EtOAc for rinsing purposes. The volume was then reduced to approximately 1 mL under a gentle flow of nitrogen.

Mucobromic acid (MBA) was added as an internal standard to each of the extracts. This was accomplished by the addition of 10 μL of a 130.5 μg/μL MBA solution in EtOAc. The concentrated extracts were methylated by the addition of 1.0 mL of a 2% sulfuric acid (v/v) in methanol solution followed by heating to 70°C for 60 minutes. Derivatized extracts were allowed to cool to room temperature and then quenched with 2 mL of 2% (m/v) sodium bicarbonate in water to obtain neutral pH. The derivatized extracts were extracted with three 1 mL portions of double distilled hexane, dried with sodium sulfate crystals and reduced to approximately 100 μL final volume by evaporation under a gentle stream of nitrogen. Concentrated final extracts were then analyzed by GC/ECD as described in the methods section.

To evaluate the efficiency of EtOAc to extract MX and EMX from carbon, three desorption steps were utilized as described in the following:

i) First extraction (desorption) The liquid remaining in the bottles containing carbon and in the sample blanks was acidified to pH ≤ 2 with 2 M sulfuric acid. Ethyl acetate (150 ± 1 mL) was added such that the bottles were headspace-free. Prior to the filling of bottles containing carbon, the glass wool plugs used as filters prior to extraction were added to the bottles. All bottles were then mixed using a rotary tumbler for nominally 1.0 day at 20°C. The complete contents of each bottle was then poured into separatory funnels with small glass wool plugs. Initially, the water layer was drained into 40 mL vials and retained. Following removal of the organic (EtOAc) layer, the glass wool plug was removed and placed in the 40 mL vial along with a small amount of Milli-Q® water at pH ≤ 2 which was used for rinsing. The EtOAc layer was passed over sodium sulfate to remove any remaining water and reduced in volume using rotary evaporation to approximately 2 mL. The extracts were transferred to 40 mL vials, derivatized and extracted with hexane in a similar manner as described earlier for the initial water (supernatant) extracts except for one difference. In these cases, the pH was adjusted only after the quenching step since the water was previously acidified to a pH ≤ 2. At this point some of the samples required more than the 2 mL of 2% sodium bicarbonate previously used to obtain neutral pH. Samples numbered 3, 5, 6, 10 and 12 all required 3 mL of sodium bicarbonate to obtain neutral pH.

Concentrated final extracts were analyzed by GC/ECD to determine both the amount of solute desorbed from the carbon and the extent of MX degradation during this first desorption step.

ii) Second extraction (desorption) The aqueous layers, glass wool filter plugs and carbon retained from the first desorption were transferred to 500 mL glass bottles (Teflon® lined screw caps) for a second desorption. EtOAc (300 mL) was added to each bottle and they were re-equilibrated at 20°C for 2.8 days. A partially filled, larger volume bottle was used in an attempt to increase desorption efficiency by providing improved mixing characteristics when compared to the first desorption step which had been conducted headspace-free.

Following equilibration, the carbon was allowed to settle by gravity since the 500 mL bottles were too large to centrifuge. 250 mL of the EtOAc layer was removed, dried, concentrated, derivatized and analyzed by GC/ECD to allow determination of the amount of solute recovered from the carbon. Prior to GC/ECD analysis, 2 to 3.5 mL of 2% sodium bicarbonate solution was added to obtain neutral pH.

iii) Third extraction (desorption) A third desorption experiment was conducted in a similar manner to the second except that 300 mL of methanol (MeOH) was used instead of EtOAc. Since water is more soluble in MeOH, it was anticipated that improved contact between the carbon and organic solvent could lead to improved solute recoveries. This third desorption experiment was equilibrated for 2.1 days at 20°C.

Approximately 10 grams of sodium sulfate were added to each bottle to remove as much of the water remaining in the mixture as was possible. The entire contents of each bottle was then filtered through a glass wool plugged separatory funnel to filter out any of the larger remaining carbon particles. The organic phase from each bottle was then passed through funnels filled with sodium sulfate to aid in further drying. This step also helped to remove carbon fines that had become more prevalent due to the extended amount of mixing that the carbon had been subjected to.

Individual organic extracts were then evaporated to dryness using a rotary evaporator. The flasks were then rinsed in two steps, first with EtOAc to be consistent with the first two desorption procedures and secondly with MeOH to remove crystals which had formed and were not soluble in EtOAc. All extracts were then subjected to the derivatization and final extraction procedures described for earlier extractions.

6.5.3.2 Results and Discussion

i) First Extraction (EtOAc) Averaged results of sample blanks 1, 5 and 9 (containing no carbon) showed that approximately 49% and 21% of the MX and EMX respectively remained following 1.0 days of equilibration (Table 6.8). This solution was originally spiked with an MX concentration of 690 μg/L and an EMX concentration of 310 μg/L. Percentage recovery of MX for the sample blanks corresponded closely to that for a sample which was spiked with nominally 500 ng/L MX+EMX (345 ng/L MX; 155 ng/L EMX). For this sample 44% of the original MX concentration was recovered following equilibration (Table 6.8).

Tables 6.9 and 6.10 list the amounts of MX and EMX recovered from carbon, respectively. Maximum recoveries averaging approximately 0.1% and 0.2% were obtained for MX and EMX respectively. These values have been corrected for contributions from the water supernatant (10 mL) which could not be separated from the carbon after the initial adsorption step and remained in the serum bottles for the first EtOAc desorption. The first extraction recoveries may have been low because the headspace-free serum bottles provided little mixing of the aqueous and organic phases. In fact it was observed that a portion of the carbon particles remained at the solvent interface and trapped in spaces of the glass wool.

ii) Second Extraction (EtOAc) Recoveries of MX from the carbon were generally much greater following the second extraction with EtOAc (Table 6.11). For the second extraction, inclusion of approximately 200 mL headspace in the 500 mL bottles provided much better aqueous/organic solvent mixing and organic solvent/carbon contact.

More EMX was recovered after the second ethyl acetate extraction than after the first extraction, and the overall percentage recovery of EMX was approximately one-third of that obtained for MX (Table 6.12). Since 10 mL (6%) of the solution volume was at pH ≤ 2, some isomerization of EMX to MX, although minor, would be expected to occur during the second and third desorption steps (Kronberg, 1987) resulting in lower EMX recoveries over time. It is also possible however, that different mechanisms govern the adsorption and possible reaction of MX and EMX with carbon.

iii) Third Extraction (MeOH) For MX, recoveries shown in Table

Table 6.9 MX Recovery Results-First Desorption Using Ethyl Acetate
(Expt. AD-88-1)

Sample/Solvent Combination (a)	Net MX Recovered From Carbon (µg) (b)	Minimum MX Recovered (%) (c)	Maximum MX Recovered (%) (d)
2 C Ext.	0.09	0.09	0.18
3 C Ext.	0.04	0.04	0.07
4 C Ext.	0.03	0.03	0.05
6 C Ext.	0.07	0.06	0.12
8 C Ext.	0.07	0.06	0.12

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial MX spike.
(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

Table 6.10 EMX Recovery Results-First Desorption Using Ethyl Acetate (Expt. AD-88-1)

Sample/Solvent Combination (a)	Net EMX Recovered From Carbon (µg) (b)	Minimum EMX Recovered (%) (c)	Maximum. EMX Recovered (%) (d)
2 C Ext.	0.02	0.04	0.19
3 C Ext.	0.02	0.04	0.21
4 C Ext.	0.02	0.04	0.17
6 C Ext.	0.02	0.04	0.21
8 C Ext.	0.02	0.04	0.18

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial EMX spike.
(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

Table 6.11 MX Recovery Results-Second Desorption Using Ethyl Acetate (Expt. AD-88-1)

Sample/Solvent Combination (a)	Net MX Recovered From Carbon (μg) (b)	Minimum MX Recovered (%) (c)	Maximum. MX Recovered (%) (d)
2 C Ext.	0.88	0.79	1.63
3 C Ext.	1.08	0.98	2.02
4 C Ext.	1.29	1.17	2.40
6 C Ext.	0.69	0.52	1.06
8 C Ext.	0.21	0.19	0.39

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial MX spike.
(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

Table 6.12 EMX Recovery Results-Second Desorption using Ethyl Acetate (Expt. AD-88-1)

Sample/Solvent Combination (a)	Net EMX Recovered From Carbon (μg) (b)	Minimum EMX Recovered (%) (c)	Maximum. EMX Recovered (%) (d)
2 C Ext.	0.06	0.12	0.57
3 C Ext.	0.05	0.10	0.47
4 C Ext.	0.11	0.22	1.06
6 C Ext.	0.04	0.07	0.34
8 C Ext.	0.04	0.09	0.42

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial EMX spike.
(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

6.13 were approximately 50% of those obtained from the first desorption using EtOAc. Results for EMX (Table 6.14) however were 2 to 3 times higher suggesting that MeOH may be a preferred solvent for use in EMX recovery.

iv) Recovery as a function of carbon dosage Recoveries of both MX and EMX are shown as a function of carbon dosage in Figures 6.19 and 6.20, respectively. With the exception of the first 19.4 mg dosage, the general trend for the second desorption suggests that recoveries are highest when carbon dosage is lowest. Thus for low doses, the carbon was more heavily loaded and thereby MX was easier to desorb. In the experiments which followed, a carbon dosage of nominally 10 mg in 160 mL was used in an effort to optimize recovery conditions.

6.5.4 Desorption Using Various Solvents (Expt. AD-88-3)

Experiment AD-88-3 was essentially a repeat of AD-88-2, which will not be reported. In experiment AD-88-2, an error was made in the initial spiking of MX and EMX such that the final concentrations were approximately 1000 times less than expected. This error made calculation of recoveries impossible since equilibrium concentrations were at or less than the detection limit.

Experiment AD-88-3 differed from experiment AD-88-1 in that two organic solvents in addition to EtOAc were evaluated for their desorption efficiencies, smaller solvent volumes were used and an initial attempt using a displacer compound was made. The solvents used in this experiment were:

Table 6.13 MX Recovery Following Third Desorption Using Methanol (Expt. AD-88-1)

Sample/Solvent Combination (a)	Net MX Recovered From Carbon (µg) (b)	Minimum MX Recovered (%) (c)	Maximum. MX Recovered (%) (d)
2 C Ext.	0.02	0.02	0.04
3 C Ext.	0.05	0.04	0.09
4 C Ext.	0.04	0.03	0.07
6 C Ext.	0.04	0.03	0.07
8 C Ext.	0.02	0.02	0.03

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial MX spike.
(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

Table 6.14 EMX Recovery Following Third Desorption Using Methanol (Expt. AD-88-1)

Sample/Solvent Combination (a)	Net EMX Recovered From Carbon (μg) (b)	Minimum EMX Recovered (%) (c)	Maximum. EMX Recovered (%) (d)
2 C Ext.	0.02	0.04	0.20
3 C Ext.	0.02	0.04	0.22
4 C Ext.	0.02	0.04	0.19
6 C Ext.	0.02	0.04	0.18
8 C Ext.	0.02	0.04	0.18

(a) All samples extracted using ethyl acetate, C=carbon extract
(b) Corrected for mL. of water present as supernatant during desorption step.
(c) Based on calculated mass of initial EMX spike.
(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

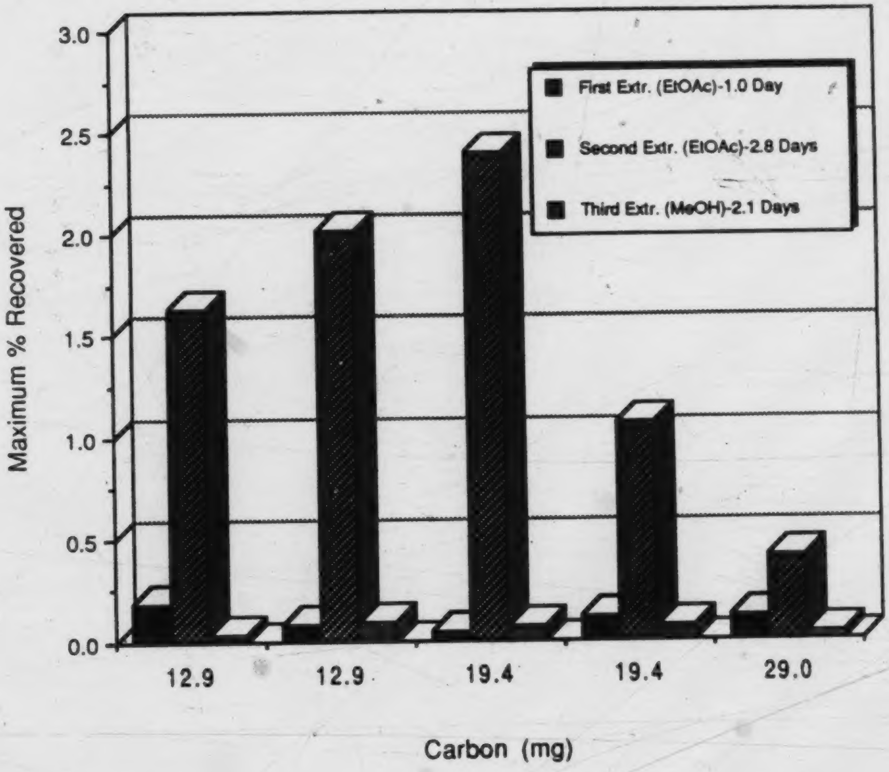


Figure 6.19 Comparison of MX Recovery Results For Three Carbon Dosages (Expt. AD-88-1)

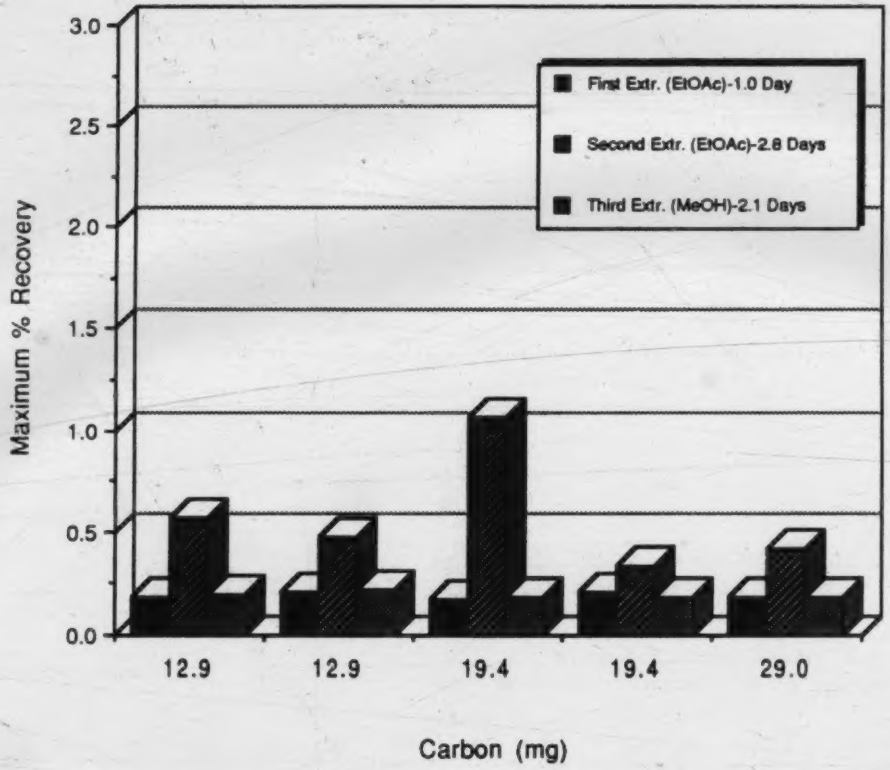


Figure 6.20 Comparison of EMX Recovery Results For Three Carbon Dosages (Expt. AD-88-1)

i) ethyl acetate (previously used in expt. AD-88-1)

ii) acetone

iii) 50:50 (v/v) dichloromethane:methanol

iv) 50:50 (v/v) dichloromethane:methanol + 0.5 g benz[a]anthracene

Reasons for the selection of these particular solvents were discussed earlier in Section 6.5.2.1.

6.5.4.1 Procedure

The procedure essentially followed that described in detail for experiment AD-88-1. Notable exceptions are described in the following paragraphs.

Upon completion of experiment AD-88-1, a new MX standard was received from the Department of Chemistry at the University of Alberta. The purity of this material was determined by GC/MS to be 96.9% MX, 3.1% EMX. As a result of the large amount of newly available MX, the initial spike concentration was increased from 1,000 μg/L to 20,000 μg/L (the concentration used in prior isotherm experiments).

To obtain a nominal concentration of 20,000 μg/L (MX+EMX), 174.1 μL of a 114.9 μg/μL standard was injected under mixing into the stainless steel delivery system which contained 1.0 L of Milli-Q® water adjusted to pH 6.0. To reduce the number of samples to be extracted only one sample blank (containing no carbon) was designated. The other four bottles contained nominally 10 mg of carbon. Exact carbon dosages are shown in Table 6.15.

Equilibration was conducted for 1.0 days at 20°C. Extraction,

Table 6.15 MX and EMX Present Following Initial Adsorption Step (Expt. AD-88-3)

Sample Designation	MX Avg. (a) (µg)	EMX Avg.(a) (µg)
1B H2O Ext. (Spiked, no carbon)	2720	0.019
2 H2O Ext. (Spiked, incl. carbon)	9.53	0.018
3 H2O Ext. (Spiked, incl. carbon)	7.74	0.018
3 H2O Ext. (Spiked, incl. carbon)	8.65	NC
5 H2O Ext. (Spiked, incl. carbon)	8.74	NC

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

NC: Not calculated since no area counts recorded.

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-11.12 mg, #3-9.04 mg, #4-10.73 mg, #5-9.14 mg.

Spike contained MX:96.9%
EMX:3.1%

concentration, derivatization and analysis were conducted as described earlier with one exception. Immediately prior to derivatization, the extracts were reduced to dryness instead of retaining 0.5 mL to 1.0 mL of solvent as in experiment AD-88-1. The internal standard (1.305 µg MBA) was added immediately prior to the occurrence of dryness. The practice of concentrating to dryness prior to derivatization, discussed in Appendix XI, was introduced to minimize the occurrence of the interference peak which may affect the delineation of the MX peak. This procedure was not implemented in experiment AD-88-1 since it may also cause a reduction in the EMX peak. In experiment AD-88-1 detection of this compound was desirable since the spike contained 31% EMX. Since the spike used in experiment AD-88-3 contained only 3.1% EMX, the determination of EMX recovery for this and further experiments was regarded as more for general interest rather than for precise quantitation.

For this experiment 25 mL of any single solvent or combination of solvents were added to 10 mL of water which remained present with the powdered carbon. Reduction in the solvent volume analyzed, from 150 mL (used in Expt. AD-88-1) to 25 mL enabled sample concentration by rotary evaporation to be accomplished in a much shorter time and allowed better mixing during the desorption step. As well, this volume was consistent with the solvent volume used in the initial extraction of the water phase to determine the MX/EMX concentration.

Desorption was allowed to occur by mixing the bottles containing solvent for 1.0 day at 20°C. Following separation and concentration of the organic layer, all extracts were taken to dryness prior to derivatization. It was necessary to filter sample number 5 twice through glass wool to remove the visible benz[a]anthracene displacer prior to concentration. A yellow precipitate was present in this sample following concentration indicating that not all of the displacer had been removed. Following derivatization all extracts were analyzed using GC/ECD to determine the amount of MX/EMX present.

To determine the effect on MX recoveries of concentrating to dryness prior to derivatization two sets of standards were prepared. In each set a known amount of MX standard was measured into a solution of 0.5 mL EtOAc which contained 10 µL of a 0.1305 µg/µL MBA solution. One set was then derivatized whereas the other set was evaporated to dryness prior to derivatization. Figure 6.21 shows a comparison of the responses obtained for the two different treatments of the standard. Additional data are provided in Appendix XV. Very little difference in response is noted in the region typically used for MX recovery calculation (MX/MBA Area Ratio 2 to 30). Therefore it appears that the determination of MX would not be adversely affected by utilizing this concentration procedure.

6.5.4.2 Results and Discussion

The sample blank (containing no carbon) measured the amount of MX degradation which occurred during the initial adsorption step. The amount of MX remaining in solution after 1.0 day equilibration was 2720 ng. Assuming a 50% degradation in 2.4 days at pH 6.0, the value of 2720 ng (Table 6.15) compared very favourably with the

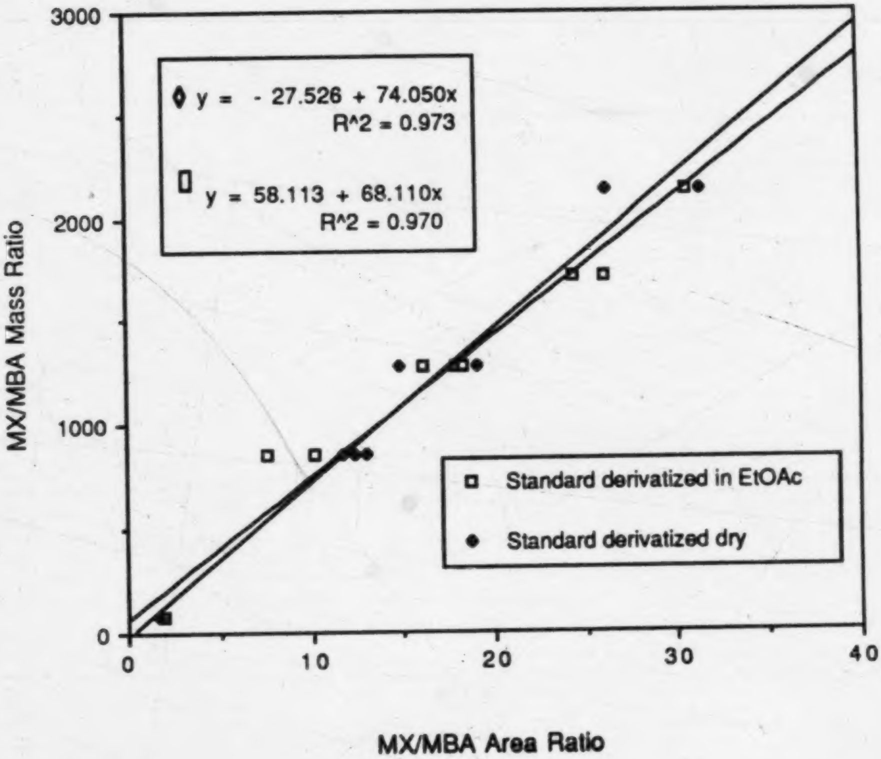


Figure 6.21 Comparison of MX/MBA Response For Two Different Concentration Methods Prior To Derivatization (Expt. AD-88-3)

expected result of 2463 ng. The amount of EMX present in the sample blank however, was much lower than normally expected, most likely attributable to the fact that all samples were taken to dryness prior to derivatization. EMX was either absent or present in very low amounts for samples which contained carbon.

Tables 6.16 and 6.17 show the amounts of MX and EMX respectively recovered from the carbon following desorption. The maximum recovery of MX (6.7%) was much greater for EtOAc in this experiment than in AD-88-1. This result is most likely due to improvements made in desorption mixing characteristics. EtOAc yielded the largest recoveries when compared with both acetone and 50% MeOH:DCM (Figure 6.22).

Acetone and 50% MeOH:DCM functioned equally well as desorption solvents but both yielded recoveries that were slightly lower than EtOAc. The low recovery of MX from 50% MeOH:DCM containing displacer may have been due in part to the insolubility of the displacer. The solution appeared supersaturated and MX may have been removed from the solvent solution by adsorption on the precipitated displacer.

No maximum percentage recovery values were calculated for EMX since the final carbon extraction values exceeded the initial blank extraction value of 0.019 μg, which was much lower than expected. An exact reason for this low value is unknown however evaporation to dryness prior to derivatization may affect the mass of EMX present in desorbed samples in a different way when compared to initial spiked-water extractions.

Minimum percentage recovery results (based on the calculated

Table 6.16 MX Recovery Following Desorption Using Various Solvents (Expt. AD-88-3)

Sample/Solvent Combination	Net MX Recovered From Carbon (µg) (a)	Minimum MX Recovered (%) (b)	Maximum. MX Recovered (%) (c)
2 C Ext. (EtOAc)	182	5.80	6.71
3 C Ext. (Acetone)	122	3.90	4.52
4 C Ext. (50%DCM/MeOH)	134	4.29	4.96
4 C Ext. (d) (50%DCM/MeOH)	49.5	1.58	1.83

C=Carbon extract

(a) Corrected for mL. of water present as supernatant during desorption step.

(b) Based on calculated mass of initial MX spike.

(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

(d) Included 0.5008 g benz[a]anthracene displacer.

Table 6.17 EMX Recovery Following Desorption Using Various Solvents (Expt. AD-88-3)

Sample/Solvent Combination	Net EMX Recovered From Carbon (µg) (a)	Minimum EMX Recovered (%) (b)	Maximum. EMX Recovered (%) (c)
2 C Ext. (EtOAc)	0.06	0.61	NR
3 C Ext. (Acetone)	0.08	0.83	NR
4 C Ext. (50%DCM/MeOH)	0.06	0.63	NR
4 C Ext. (d) (50%DCM/MeOH)	0.06	0.64	NR

C=Carbon extract

(a) Corrected for mL. of water present as supernatant during desorption step.

(b) Based on calculated mass of initial EMX spike.

(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

(d) Included 0.5008 g benz(a)anthracene displacer.

NR: Not reported since final carbon extraction values exceed initial blank extraction value of 0.019 µg, which was much lower than expected.

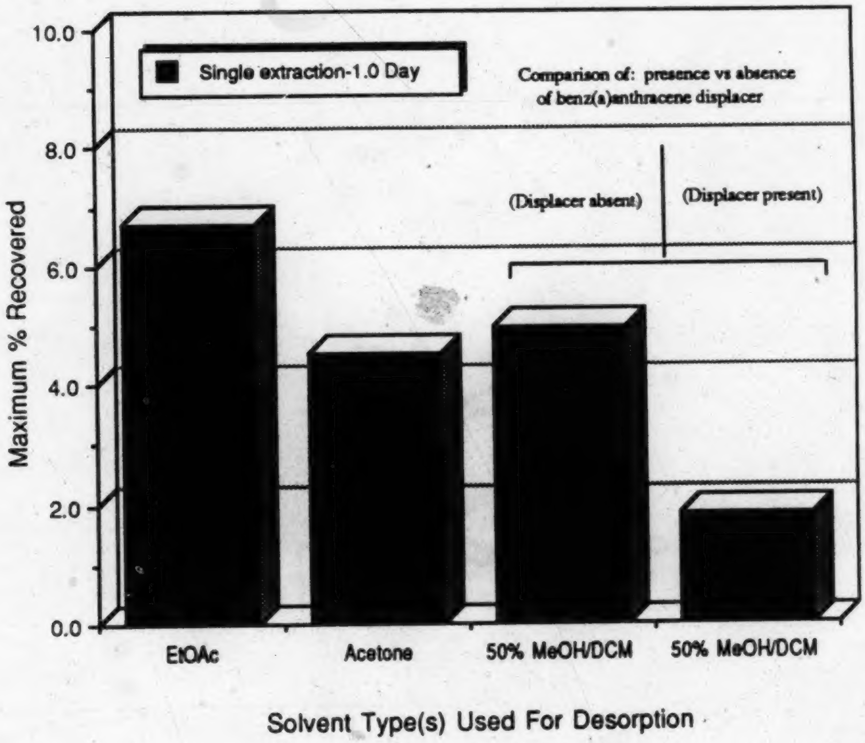


Figure 6.22 Comparison of MX Recovery Efficiencies For Various Solvent Types (Expt. AD-88-3)

EMX spike value) were approximately an order of magnitude higher than observed in experiment AD-88-1. This supports the results obtained for MX recoveries, suggesting that the changes in the desorption method improved recoveries, despite any possible reduction in EMX concentration attributed to reducing extracts to dryness.

6.5.5 Desorption Using Various Solvents + 1.5g Displacer (Experiment AD-88-4)

The purpose of conducting this experiment was to gain information regarding the effectiveness of using benz[a]anthracene-7,12-dione as a displacer. The experimental design was essentially the same as for experiment AD-88-3 except that benz[a]anthracene-7,12-dione had been located and was obtained for use as the displacer instead of benz[a]anthracene. The effectiveness of the displacer in combination with each of three organic solvents (ethyl acetate, acetone and a 50% mixture of MeOH:DCM) for removing MX from carbon was investigated.

In addition to the main experiment, two minor experiments were also conducted. One of these further evaluated the effect of taking supernatant extracts from the desorption step to dryness prior to derivatization. The other compared the effect of filtering derivatized extracts through syringes equipped with Teflon® filters (0.45 µm-Acro LC35, Gelman Sciences, Canada) to remove residual benz[a]anthracene,7-12-dione prior to GC injection.

6.5.5.1 Procedure

The experimental parameters used in experiment AD-88-4 are shown in Table 6.18.

A solution of buffered (pH 6.13) Milli-Q® water was prepared containing 19674 µg/L and 629 µg/L of MX and EMX respectively. In addition to the sample blank containing no carbon, two other "blanks" were included as shown in Table 6.18. The water blank contained buffered water only. This blank was used as a check to determine if a small interference peak which occured near the MX peak identified in a previous experiment (AD-88-1) was in fact MX. The carbon blank contained only buffered water and 10.8 mg carbon. This blank was used as a check to ensure that no peaks originating from the virgin carbon were being reported as MX or EMX.

Equilibration was conducted for 1.0 days at 20°C. Extraction, concentration, derivatization and analysis were conducted as described in Section 6.5.4.1 except that not all supernatant extracts were taken to dryness.

To determine the effect of taking supernatant extracts to dryness prior to derivatization, both the sample blank and sample number 2 were split into two equal volumes of approximately 0.5 mL prior to derivatization. These samples were chosen for comparison because they represented the two extremes in MX/EMX concentration normally encountered in an adsorption/desorption experiment.

To reduce the amount of MX/EMX associated with extraneous water remaining with the carbon prior to addition of solvent, as much water as possible was removed from bottles which contained carbon using a Pasteur pipet. The volume of water removed was

Table 6.18 Experimental Parameters For Experiment AD-88-4

Sample No.	Reference Designation	Mass Carbon) (mg)	Adsorbate Solution Type
1B	sample blank	0.0	spiked (MX/EMX)
2	sample	11.0	spiked (MX/EMX)
3	sample	10.9	spiked (MX/EMX)
4	water blank	0.0	buffered water only
5	sample	9.6	spiked (MX/EMX)
6	Carbon blank	10.8	buffered water only

measured using a 10 mL graduated cylinder and recorded such that the exact amount remaining in the bottle could be calculated. Typically 7 to 8 mL could be carefully removed without disturbing the carbon which had been centrifuged to the bottom.

The three solvents (EtOAc, acetone and 50% MeOH:DCM) were prepared such that they each contained 1.5 g of benz[a]anthracene-7,12-dione displacer per 25 mL. This was the same volume of solvent and displacer concentration used by Thakkar and Manes (1987, 1988) to displace priority pollutants from Filtrasorb 400® carbon. The volume of solvent (25 mL) added to each bottle was the same as in experiment AD-88-3. This allowed recoveries with and without displacer to be directly compared (AD-88-1 vs AD-88-3).

Desorption was conducted for 2.0 days at 20°C as suggested by Thakkar and Manes (1987). It was hoped that by extending the desorption period to two times the length previously used, displacement by the benz[a]anthracene-7,12-dione would improve recoveries.

Following desorption, 10 mL of organic layer was separated and filtered but not concentrated. Use of 0.5 g of the displacer per 25 mL solvent in experiment AD-88-3 had shown that a large amount of precipitate formed upon concentration. For this reason, 10 mL of each organic layer was derivatized directly by adding 10 μL of 130.5 ng/μL MBA (internal standard), 10 mL of 2% sulfuric acid in MeOH and mixing for 1 hour at 73°C in a temperature controlled shaker oven (Technical Services Department, University of Alberta).

The derivatized contents of each bottle was then allowed to cool to room temperature, transferred to a 125 mL separatory funnel and pH adjusted to neutral by the addition of 20 mL of 2% sodium bicarbonate. The derivatives were then extracted using three 10 mL portions of hexane. Individual hexane extracts were then combined in 50 mL round bottom flasks and concentrated using rotary evaporation. Concentrates were then transferred to 1 dram (3.7 mL) vials where they were further reduced under nitrogen to approximately 100 µL. The presence of displacer precipitate at this point suggested that filtration prior to analysis would be required to minimize contamination of the system. For this purpose, small Teflon® filters (0.45 µm) were attached to the end of a glass syringe. The filtrate was transferred to a clean 1 dram vial. Approximately 1 mL of hexane was then added to the original vial for rinsing purposes. This remaining solvent was then filtered and transferred to a new vial. Concentration was once again conducted under nitrogen to a volume of approximately 100 µL.

To assess any impacts resulting from this filtration step, sample number 5 was analyzed both before and after filtration.

As a result of derivatizing in 10 mL of solvent containing displacer instead of dry or containing 0.5 to 1 mL solvent, construction of a new response curve was required which reflected these changes.

The solution used for standards was prepared in a 160 mL serum bottle by adding 50 mL of EtOAc and enough benz[a]anthracene-7,12-dione to completely saturate the solution. 10 mL aliquots of this solution were measured into each of four 50 mL serum bottles. To each bottle 10 µL of 130.5 ng/µL MBA, 10 mL sulfuric acid and 1 to 5 µL of a 11.49 µg/µL MX standard to cover the anticipated range of recoveries. The bottles were then heated in the shaker oven, allowed to cool, pH adjusted with 2% sodium bicarbonate and extracted with three 10 mL aliquots of hexane as described earlier for treatment of the actual samples. The organic extracts were then concentrated using rotary evaporation, transferred to 1 dram vials and further concentrated to approximately 100 µL under nitrogen. These standards were then directly analyzed by GC/ECD and were not filtered as previously described due to the low amount of residual displacer present. The large volume derivatization (LVD) response curves resulting from this exercise are shown in Figures XV.7 and XV.8, Appendix XV.

6.5.5.2 Results and Discussion

Results of the initial supernatant extraction are shown in Table 6.19. The amount of MX remaining in solution after 23.5 hours of equilibration following a dry-derivatization procedure was 2729 µg. This value compared very closely to the 2503 µg predicted from kinetics data for an equilibration time of 1.0 day.

Results comparing dry as opposed to solvated derivatization for the sample blank are shown in Table 6.19 and Figure 6.23. Less than a 4% difference was noted in the concentration of MX, however as expected, a large decrease was noted in the mass of EMX present in the extract which was taken to dryness.

Similar results are shown for the supernatant measured in sample H2O-2 (bottle number 2) which contained 11.0 mg of carbon (Table 6.19, Figure 6.24). Less than a 0.03% difference was noted in the concentration of MX when the two extract concentration

Table 6.19 MX and EMX Present Following Initial Adsorption Step (Expt. AD-88-4)

Sample Designation	MX Avg. (a) (μg)	EMX Avg.(a) (μg)
1 H_2O Ext. (Spiked, no carbon)	2730	11.6
1 H_2O Ext. (Spiked, no carbon) (b)	2830	0.020
2 H_2O Ext. (Spiked, incl. carbon)	7.47	0.019
2 H_2O Ext. (Spiked, incl. carbon) (b)	7.47	0.018
3 H_2O Ext. (Spiked, incl. carbon)	7.47	0.020
4 H_2O Ext. (Water blank)	NC	NC
5 H_2O Ext. (Spiked, incl. carbon)	7.48	0.021
6 H_2O Ext. (Carbon blank)	NC	NC

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.
(b) Sample taken to dryness prior to derivatization.

NC: Not calculated since no area counts recorded.

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-11.0 mg, #3-10.9 mg, #5-9.6 mg, #6-10.8 mg.

Spike contained MX:96.9%
EMX:3.1%

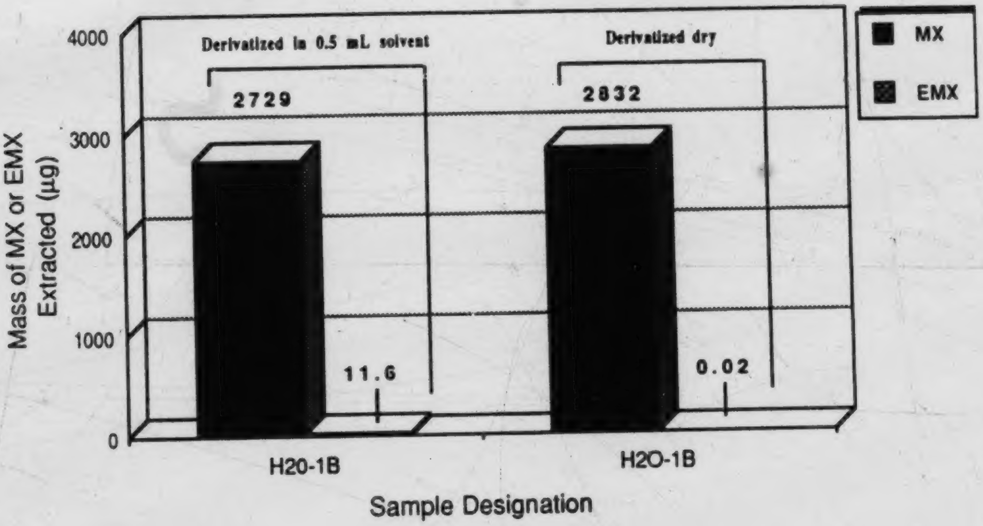


Figure 6.23 Comparison of MX and EMX Extraction Results For Sample Blanks Using Two Different Concentration Methods Prior To Derivatization (Expt. AD-88-4)

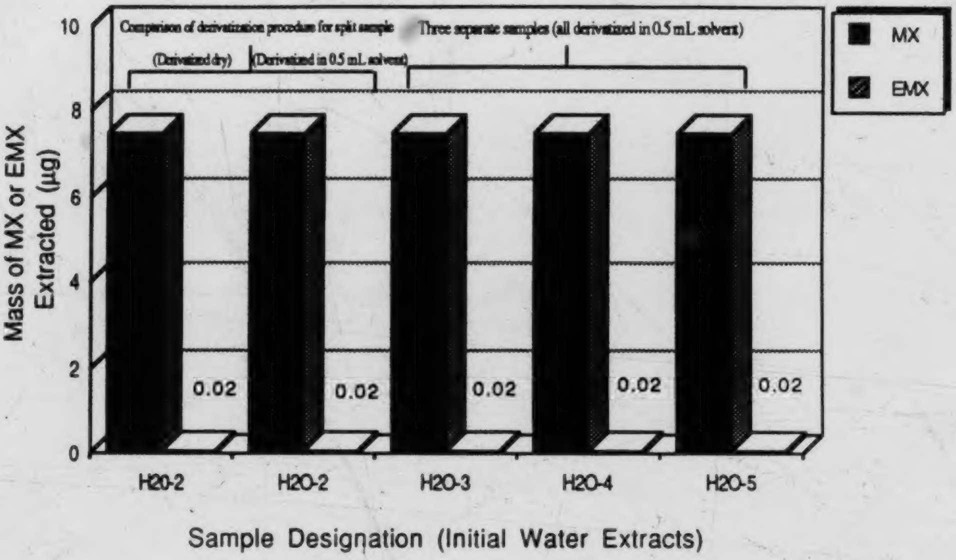


Figure 6.24 Comparison of MX and EMX Extraction Results For Supernatants Using Two Different Concentration Methods Prior To Derivatization (Expt. AD-88-4)

treatments were compared. The residual mass of MX present in sample H2O-2 was shown to be typical of all bottles which contained carbon (Figure 6.24). Values of EMX bordered on the detection limit for this experiment.

Residual mass values of approximately 7.5 µg determined for bottles containing both MX/EMX and carbon indicated that almost the entire mass of MX initially spiked into the bottles was removed by the carbon. Theoretically, anywhere between 2721 and 3140 µg of MX had been loaded onto the carbon during the initial adsorption equilibrium period assuming adsorption was responsible for the removal of MX as opposed to some irreversible reaction mechanism.

No MX was detected in the carbon blank which contained only carbon and buffered water. A small peak observed at the same relative retention time as MX in the water blank sample (containing only buffered water) was determined by GC/MS not to be MX. It was a very small peak and would not have contributed significantly to the MX peak at the concentrations of MX being measured in the experiment. As well, it appeared that carbon was capable of removing it since there was no such peak in the carbon blank.

Recovery of MX and EMX.

Desorption recovery results for MX and EMX using various solvents (including displacer) are shown in Tables 6.20, 6.21 and Figure 6.25. Both acetone and 50% MeOH:DCM provided similar recoveries in combination with displacer while the EtOAc/displacer solution removed less MX from the carbon. The similarity between recoveries using acetone and 50% MeOH:DCM solvents were directly

Table 6.20 MX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-Dione Displacer (1.5 g/25 mL) (Expt. AD-88-4)

Sample/Solvent Combination	Net MX Recovered From Carbon (µg) (a)	Minimum MX Recovered (%) (b)	Maximum. MX Recovered (%) (c)
2 C Ext. (EtOAc)	17.3	0.55	0.63
3 C Ext. (Acetone)	29.8	0.95	1.09
5 C Ext. (50%DCM/MeOH)	28.9	0.92	1.06
5 C Ext. (d) (50%DCM/MeOH)	26.9	0.86	0.99

C=Carbon extract

(a) Corrected for mL. of water present as supernatant during desorption step.

(b) Based on calculated mass of initial MX spike.

(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

(d) Sample not filtered, all others passed through Teflon® filters prior to GC analysis.

Table 6.21 EMX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-Dione Displacer (1.5 g/25 mL) (Expt. AD-88-4)

Sample/Solvent Combination	Net EMX Recovered From Carbon (µg) (a)	Minimum EMX Recovered (%) (b)	Maximum. EMX Recovered (%) (c)
2 C Ext. (EtOAc)	0.43	0.43	3.74
3 C Ext. (Acetone)	0.39	0.38	3.34
5 C Ext. (50%DCM/MeOH)	0.37	0.38	3.29
5 C Ext. (d) (50%DCM/MeOH)	0.38	0.38	3.30

C=Carbon extract

(a) Corrected for mL. of water present as supernatant during desorption step.

(b) Based on calculated mass of initial EMX spike.

(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

(d) Sample not filtered, all others passed through Teflon® filters prior to GC analysis.

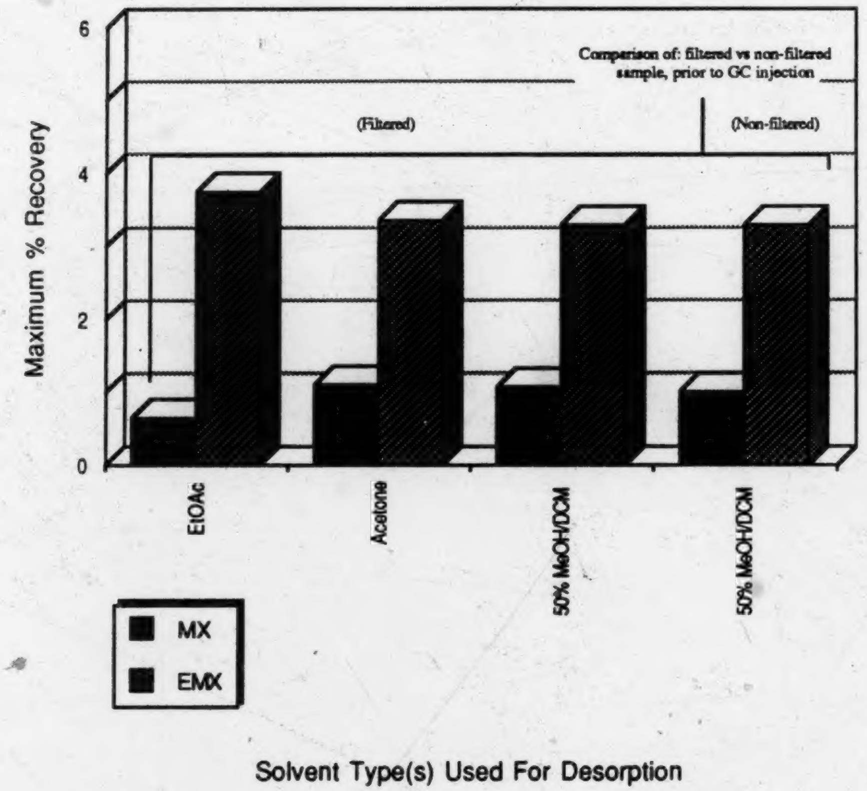


Figure 6.25 Comparison of MX and EMX Recovery Efficiencies Using Benz[a]anthracene-7,12-Dione Displacer and Various Solvent Types (Expt. AD-88-4)

comparable with results obtained in experiment AD-88-3. However, recoveries reported for experiment AD-88-3 were approximately 5 to 6 times higher for those solvents. The lower recoveries of MX may have been in part, attributable to the insolubility of the displacer in all of the solvents. MX may have been adsorbed on the displacer precipitate present in the solutions, all of which were supersaturated. This hypothesis may also be supported by results which show that an increase in displacer from experiment AD-88-3 to AD-88-4 (0.5 g/25 mL to 1.5 g/25 mL) correlated with a decrease in recoveries. Lower recoveries in experiment AD-88-4 for similar solvents may also have been due, in part, to the large volume derivatization method (10 mL as opposed to 1 mL) necessitated by the higher displacer concentration. In contrast to experiment AD-88-3, EtOAc provided lower recoveries that either acetone or 50% MeOH:DCM. Again, this may be attributable to interaction with the precipitate.

In general, EMX recovery results were similar to those reported for MX except that the highest recoveries were for the desorption using EtOAc.

6.5.6 Desorption Using Various Solvents + 0.005g Displacer (Experiment AD-89-5)

The primary objective of this experiment was to reevaluate the use of benz[a]anthracene-7,12-dione as a displacer by using a different dosage criterion. For this experiment the concentration of the displacer was reduced from 1.5 g/25 mL used previously (Experiment AD-88-4) to 0.005 g/25 mL. Solubility tests conducted using the solvents EtOAc, acetone and 50% MeOH:DCM had shown that approximately 0.005 g of displacer would dissolve without supersaturating the solution and forming a precipitate. Advantages associated with using the lower displacer concentration included:

i) less likelihood of MX/EMX adsorption onto precipitate,

ii) elimination of large volume (10 mL) derivatizations, including standards required to determine ECD detector response, and

iii) elimination of derivatized extract filtration step (using Teflon® filters) prior to GC/ECD analyses.

Each of these advantages should cause a reduction in possible losses of MX/EMX and lead to higher recoveries.

Results for experiment AD-88-4 had shown that concentration to dryness prior to derivatization did not adversely affect the measurement of MX but could in some instances (especially at high concentrations) reduce the recovery efficiency of EMX. Since the accurate measurement of MX was of primary importance, the practice of concentration to dryness was adopted for both this experiment and experiment AD-89-6. For this reason desorption recoveries of EMX should be viewed with caution, despite the use of dry-derivatization response curves (MX and EMX) for both of these experiments.

6.5.6.1 Procedure

For this experiment only, buffered (pH 6.03) Milli-Q® water was prepared containing 9,714 µg/L MX and 311 µg/L EMX. These low values resulted from an error in spiking which yielded concentrations 50% less than typically used.

Equilibration during the adsorption step was conducted at 0.7 days at 20°C.

In addition to the three solvents normally used for desorption (EtOAc, acetone and 50% MeOH:DCM), 7 % MeOH:DCM was also included. This was the same solvent mixture used by Thakkar and Manes (1987) in conjunction with displacer for desorption of priority pollutants.

The serum bottle volume used during desorption was reduced from 160 mL to 50 mL to provide improved contact between the organic and aqueous phases and to reduce the glass surface area available for possible adsorption of MX.

An initial desorption equilibration time of 1.0 day was used for all solvents. For the 50% MeOH:DCM mixture, a separate bottle designated as 6A in Table 6.22 was allowed to desorb for a period of two days. In previous experiments (AD-88-3, AD-88-4) this solvent combination has produced consistently good recoveries. It was also the only solvent in which displacer had previously been added in varying concentrations (0.5 g/25 mL in experiment AD-88-3, 1.5 g/25 mL in experiment AD-88-4). The combination of using both a third displacer concentration and two desorption equilibration times allowed the effect of these variables to be assessed more fully.

6.5.6.2 Results and Discussion

Results of the initial adsorption step are shown in Table 6.22. As expected, very low concentrations of MX remained in sample bottles which contained carbon. The lower than usual residual

Table 6.22 MX and EMX Present Following Initial Adsorption Step (Expt. AD-89-5)

Sample Designation	MX Avg. (a) (µg)	EMX Avg.(a) (µg)
1B H2O Ext. (Spiked, no carbon)	640	3.95
2 H2O Ext. (Spiked, incl. carbon)	0.078	0.019
3 H2O Ext. (Spiked, incl. carbon)	0.025	0.019
4 H2O Ext. (Spiked, incl. carbon)	0.014	0.019
6 H2O Ext. (Spiked, incl. carbon)	0.296	0.022
6A H2O Ext. (Spiked, incl. carbon)	0.038	0.019

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-9.6 mg, #3-10.6 mg, #4-10.6 mg, #6-11.0 mg.,#6A-11.0 mg.

Spike contained MX:96.9%
EMX:3.1%

sample blank concentration (sample 1B) reflected the lower initial starting mass of only 1,554 µg/160 mL.

Desorption recovery results are shown in Tables 6.23 and 6.24 for MX and EMX respectively, and summarized in Figure 6.26. For one day desorptions, the solvent combination of 7% MeOH:DCM (including displacer) provided the best recovery of MX (5.8%) removing more than twice as much when compared to 50% MeOH:DCM, the next most efficient solvent (Table 6.23). The 50% MeOH:DCM combination provided an extraction efficiency which was higher than in any previous experiment involving the use of a displacer.

Recoveries of EMX were higher than observed in previous experiments, despite taking extracts to dryness prior to derivatization. For the one day desorption period maximum recoveries ranged from 1.1 to 1.4%.

Results which directly compare desorption times of one and two days are shown in Figure 6.26 for the solvent combination of 50% MeOH:DCM. For these samples, a five times increase was noted for the recovery of MX for a two-fold increase in desorption time. A maximum recovery of 10.7% of the original MX present was the largest observed in any experiment.

The effect of varying displacer concentration and desorption time on MX recovery are summarized in Table 6.25 for the solvent combination of 50% MeOH:DCM. Inclusion of a displacer was shown to be detrimental for one day desorption times. However a decrease in displacer from 1.5 g/25 mL to 0.005 g/25 mL was shown to improve desorption efficiency, possibly due to less adsorption of MX on any precipitate that may have been present. For conditions

Table 6.23 MX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-Dione Displacer (0.005 g/25 mL) (Expt. AD-89-5)

Sample/Solvent Combination	Net MX Recovered From Carbon (μg) (a)	Minimum MX Recovered (%) (c)	Maximum. MX Recovered (%) (d)
2 C Ext. (EtOAc)	14.2	0.46	2.22
3 C Ext. (Acetone)	3.64	0.12	0.57
4 C Ext. (b) (7%DCM in MeOH)	36.9	1.19	5.77
6 C Ext. (50%DCM/MeOH)	15.3	0.49	2.39
6A C Ext. (e) (50%DCM/MeOH)	68.1	2.19	10.7

C=Carbon extract

(a) Corrected for mL of water present as supernatant during desorption step.

(b) Correction factor as per (a) not applied since water separated into a distinct phase.

(c) Based on calculated mass of initial MX spike.

(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

(e) This sample was desorbed for 2 days, all others desorbed for 1 day.

Table 6.24 EMX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-Dione Displacer (0.005 g/25 mL) (Expt. AD-89-5)

Sample/Solvent Combination	Net EMX Recovered From Carbon (µg) (a)	Minimum EMX Recovered (%) (c)	Maximum. EMX Recovered (%) (d)
2 C Ext. (EtOAc)	0.05	0.49	1.24
3 C Ext. (Acetone)	0.05	0.47	1.19
4 C Ext. (b) (7%DCM in MeOH)	0.05	0.46	1.14
6 C Ext. (50%DCM/MeOH)	0.05	0.55	1.39
6A C Ext. (e) (50%DCM/MeOH)	0.05	0.53	1.34

C=Carbon extract

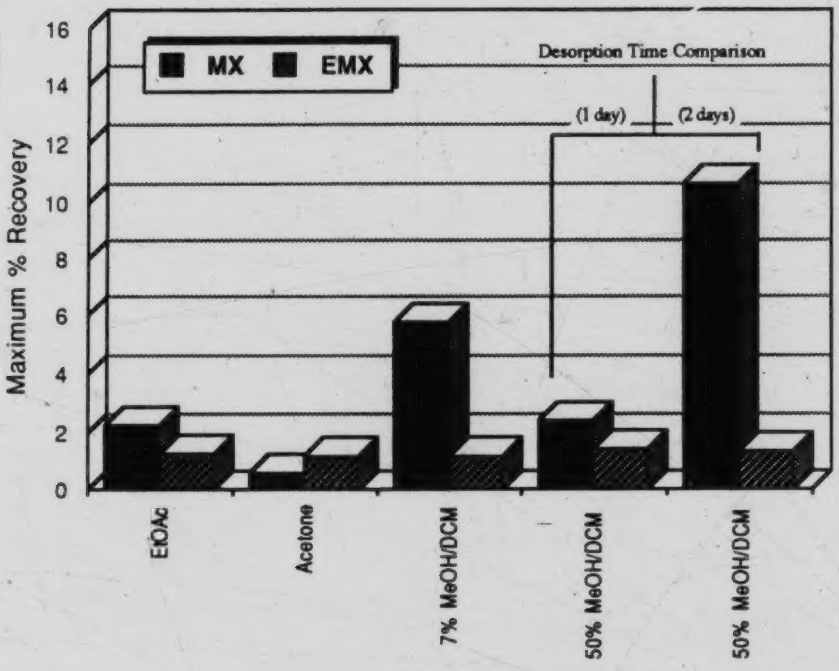
(a) Corrected for mL of water present as supernatant during desorption step.

(b) Correction factor as per (a) not applied since water separated into a distinct phase.

(c) Based on calculated mass of initial EMX spike.

(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

(e) This sample was desorbed for 2 days, all others desorbed for 1 day.



Solvent Type(s) Used For Desorption

Figure 6.26 Comparison of MX Recovery Efficiencies Using Benz[a]anthracene-7,12-Dione Displacer and Various Solvent Types For Two Desorption Periods (Expt. AD-89-5)

Table 6.25 MX and EMX Recoveries Showing Effect of Varying Benz[a]anthracene-7,12-Dione Displacer Concentration (Expt. AD-89-5)

Experiment Designation	Displacer Added (g/25 mL of solvent)	Max. MX Recovered (%)
AD-88-3	0.0	5.0
AD-88-3 (a)	0.5	1.8
AD-88-4 (b)	1.5	1.1
AD-88-5	0.005	2.4
AD-88-5	0.005	10.7 (c)

(a) Displacer used was benz[a]anthracene, not benz[a]anthracene-7,12-dione as in all others.

(b) Utilized large volume derivatization (10 mL), all others used normal normal derivatization procedure.

(c) Two day desorption period, all others one day.

tested, optimal desorption efficiency was obtained using 0.005 g/25 mL of displacer and a desorption time of two days. The same desorption period without displacer however was not examined.

6.5.6.3 GC/MS Analyses of Desorbed MX

Two peaks which appeared in ECD chromatograms of activated carbon desorbates and were similar in size to the recovered MX peak warranted further investigation by GC/MS. These peaks were absent from carbon blanks and MX blanks but they could be observed in MX standards of very high concentration and therefore were thought to be natural transformation products of MX. Measurements of GC/ECD peak area ratios relative to the internal standard suggest that MX transformation was enhanced in the presence of activated carbon. Table 6.26 shows that while peak area ratios of these unknowns are very small in blanks and standards, they increase to the same order of magnitude as that of recovered MX for samples containing carbon. As well, Table 6.26 shows that while an increase in desorption time from 1 to 2 days resulted in a 3.3 times increase in the recovery of MX, the recovery of one unknown (U1) decreased by 0.88 and the other peak (U2+U3) only increased by 1.2 times. The interpretation of these results in terms of the adsorptive strengths of compounds U1 and U2/U3 is difficult because it is not known what the total amount of these compounds present on the carbon was, and therefore what percentage was recovered. It is also possible that catalyzed MX decomposition is slower than MX desorption, although the low overall MX recoveries obtained preclude definite conclusions at this time.

Table 6.26 Area Ratios for MBA, MX and Unknown Peaks for Two Solvent Extraction Conditions

Peak Area Ratios					
	Standards			Solvent Extractions (50% MeOH:DCM)	
Peak	16 µg std	1663 µg std	Carbon Blank	(1 Day)	(2 Days)
MX	319	1444*	316	81	267
U1	0.10	3.98	0.09	136	120
U2+U3	13	105	1.15	59	73

U1-Unknown #1, measured @ GC/ECD RT 8.4 min.
U2+U3-Unknown #2 and #3 (unresolvable), measured @ GC/ECD RT 10.9 min.
*Peak offscale.

GC/MS analysis allowed resolution of the second GC/ECD peak into two peaks and provided mass spectra for all three peaks (Figure 6.27) consistent with the structures shown in Figure 6.28. These structures are chlorinated compounds with some similarities to MX, their mutagenic properties are unknown. Authentic standards for these compounds were unavailable and prevented direct quantitation of these MX transformation products.

6.5.7 Desorption Using High Temperature (70°C) (Experiment AD-89-6)

Previous experiments had shown that for one day desorption periods the presence of a displacer compound did not significantly enhance recovery of MX from carbon. The objective of this, the last of a series of desorption experiments, was to eliminate the addition of displacer and attempt to increase recovery by increasing the temperature at which desorption was conducted. Temperatures above ambient have been applied by others to enhance recovery of organic compounds from activated carbon. Loper et al. (1985) used DCM as a solvent in combination with Soxhlet apparatus to remove mutagenic substances from granular activated carbon, however the temperature required for refluxing was not stated. Application of a similar method described in Section 5.4 was found successful for removing MX from carbon however again, the temperature required to obtain 4 cycles per hour was not recorded. Jackson et al. (1987) evaluated recovered reaction products formed from the reaction of resorcinol with chlorine and chlorine dioxide in the presence of activated carbon. For these experiments carbon was Soxhlet

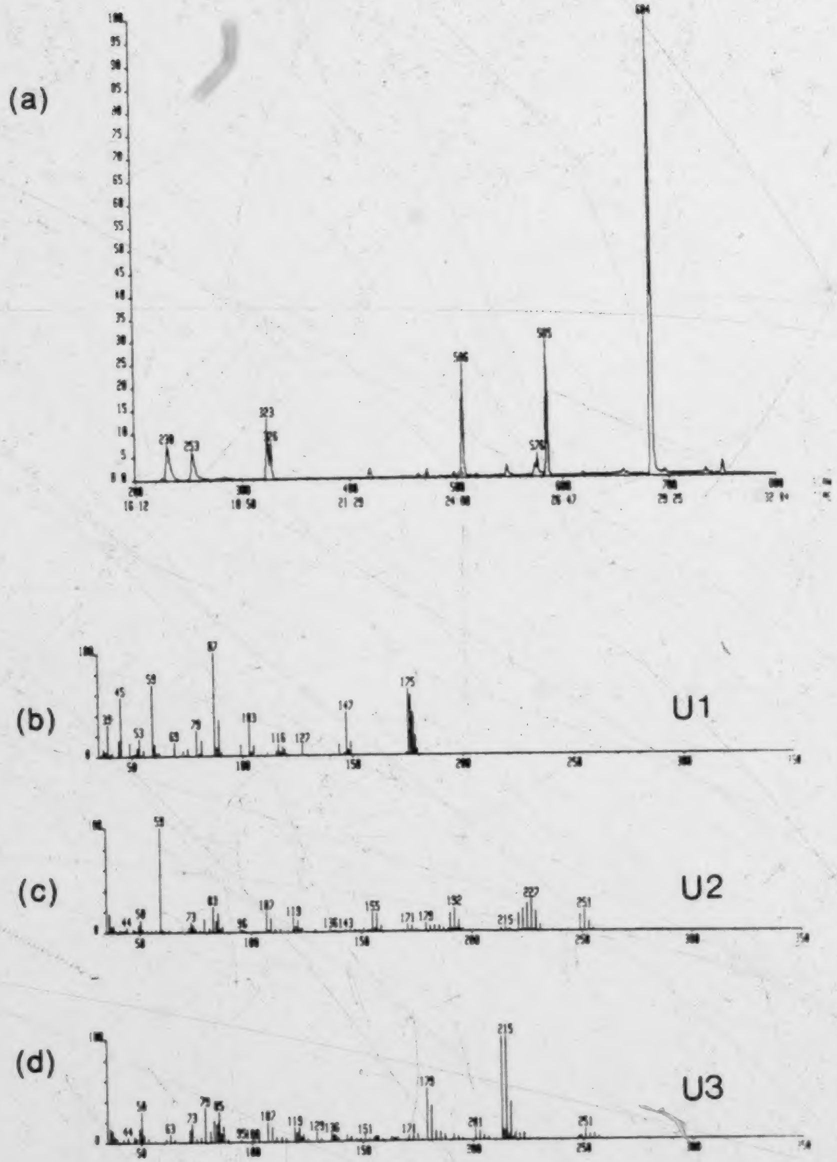
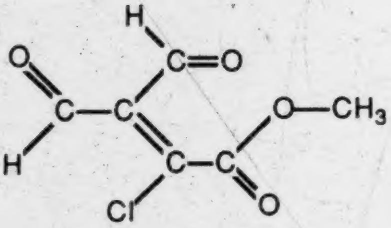
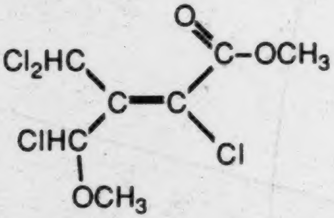


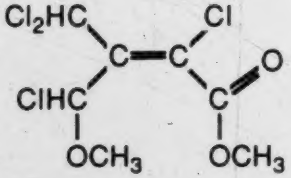
Figure 6.27 Total Ion Current Chromatogram (a) for 50% Methanol in Dichloromethane Extract of PGAC Loaded with MX, and Mass Spectra (b), (c), (d) of Three Compounds Not Observed in Blanks



(a) U1: Methyl ester of 2-chloro-3-carboxy-4-oxo-butenoic acid



(b) U2: E-2,4-dichloro-3-(dichloromethyl)-4-hydroxy-2-butenoic acid



(c) U3: Z-2,4-dichloro-3-(dichloromethyl)-4-hydroxy-2-butenoic acid

Figure 6.28 (a) Structure Consistent with the Mass Spectrum of Figure 6.27 (b), (b) Stucture Consistent with the Mass Spectrum of Figure 6.27(c), (c) Stucture Consistent with the Mass Spectrum of Figure 6.27(d) extracted with a mixture of 50% MeOH:DCM, however as in experiments conducted by Loper et al. (1984), the temperature was not recorded. Ho and Daw (1988) reported that for batch experiments maintaining a temperature of 70°C during desorption with the organic solvents acetone and methanol resulted in a range of 81 to 95% recovery of 2,4-dinitrotoluene from powdered Filtrasorb 300® and Filtrasorb 400® carbons. Significant increases in extraction efficiency were observed when extractions conducted at room temperature were compared with those conducted at 70°C.

A temperature of 70°C, selected for batch recovery of MX from carbon using DCM (b.p. 40°C) was at or above temperatures involved in Soxhlet extractions used by others and in agreement with batch experiments conducted by Ho and Daw (1988) involving acetone and methanol. It was also the temperature recommended for the derivatization of MX, therefore by not exceeding this temperature adverse thermal decomposition effects could be minimized.

Kronberg (1987) stated that at 60°C, pH ≤ 2.0 MX decomposition would occur, however no rate data was reported. To reduce any associated losses of MX due to decomposition at high temperature (70°C), desorption was conducted for a period of only 0.9 days.

6.5.7.1 Procedure

To allow for possible thermal decomposition of MX during desorption at 70°C and ensure measurable recovery amounts, the initial concentration was increased a factor of ten from experiment AD-89-5. Buffered (pH 6.03) Milli-Q® water was prepared containing a concentration of 91,149 µg/L MX and 3,108 µg/L EMX.

The adsorption step was conducted for 0.9 days at 20°C.

Solvents used for desorption were the same as described for experiment AD-89-5, these included EtOAc, acetone, 7% MeOH:DCM and 50 % MeOH:DCM. As a further attempt to increase solvent extraction efficiency, 100 mL of solvent (instead of 50 mL used in experiment AD-88-4) was added directly to the 160 mL serum bottle following removal of the 150 mL water required for the initial (adsorption phase) extraction, and as much remaining extraneous water as possible. To ensure that pH ≤ 2 was obtained prior to desorption equilibration 16 drops of 2 M sulfuric acid was added to each bottle. All bottles were then placed in a shaker/incubator at 70°C for a period of 0.9 days. Use of the shaker/incubator was required since a temperature of 70°C could not be attained in the temperature controlled cold room which housed the rotary tumbler normally used for desorption.

6.5.7.2 Results and Discussion

Initial adsorption liquid phase results are shown in Table 6.27. As expected, residual (supernatant) MX concentrations were approximately a factor of ten higher that observed in experiment AD-89-5 due to the increase in the initial spiked concentration. Desorption recovery results for MX and EMX are reported in Tables 6.28 and 6.29 respectively and summarized in Figure 6.29.

The 7% MeOH:DCM solvent combination yielded the highest maximum recovery of MX (5.3%) of the four solvents evaluated. This value compared very closely to the 5.8% obtained for the same solvent (containing 0.005g/25 mL displacer) in experiment AD-89-5.

Table 6.27 MX and EMX Present Following Initial Adsorption Step (Expt. AD-89-6)

Sample Designation	MX Avg. (a) (μg)	EMX Avg.(a) (μg)
1 H2O Ext. (Spiked, no carbon)	7410.	4.14
2 H2O Ext. (Spiked, no carbon)	7200.	4.56
3 H2O Ext. (Spiked, incl. carbon)	6.69	0.02
4 H2O Ext. (Spiked, incl. carbon)	1.63	0.02
5 H2O Ext. (Spiked, incl. carbon)	1.91	0.02
6 H2O Ext. (Spiked, incl. carbon)	5.35	0.03
7 H2O Ext. (Spiked, incl. carbon)	4.97	0.03
8 H2O Ext. (Spiked, incl. carbon)	4.25	0.02

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #3-9.9 mg, #4-9.8 mg, #5-10.1 mg, #6-10.8 mg, #7-10.6 mg,#8-10.9 mg,#9-10.9 mg.

Spike contained MX:96.9%
EMX:3.1%

Table 6.28 MX Recovery Following Desorption at 70°C Using Various Solvents (Expt. AD-89-6)

Sample/Solvent Combination	Net MX Recovered From Carbon (µg) (a)	Minimum MX Recovered (%) (c)	Maximum MX Recovered (%) (d)
4 C Ext. (EtOAc)	240	1.5	3.3
5 C Ext. (Acetone)	83.1	0.5	1.1
7 C Ext. (b) (7% MeOH/DCM)	390	2.5	5.3
8 C Ext. (50% MeOH/DCM)	183	1.2	2.5

C=Carbon extract

(a) Corrected for mL of water present as supernatant during desorption step.

(b) Correction factor as per (a) not applied since water separated into a distinct phase.

(c) Based on calculated mass of initial MX spike.

(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

Table 6.29 EMX Recovery Following Desorption at 70°C Using Various Solvents (Expt. AD-89-6)

Sample/Solvent Combination	Net EMX Recovered From Carbon (μg) (a)	Minimum EMX Recovered (%) (c)	Maximum. EMX Recovered (%) (d)
4 C Ext. (EtOAc)	NVD	NVD	NVD
5 C Ext. (Acetone)	0.05	0.0	1.1
7 C Ext. (b) (7% MeOH/DCM)	0.08	0.0	1.8
8 C Ext. (50% MeOH/DCM)	NVD	NVD	NVD

C=Carbon extract

(a) Corrected for mL of water present as supernatant during desorption step.

(b) Correction factor as per (a) not applied since water separated into a distinct phase.

(c) Based on calculated mass of initial EMX spike.

(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

NVD: No value determined.

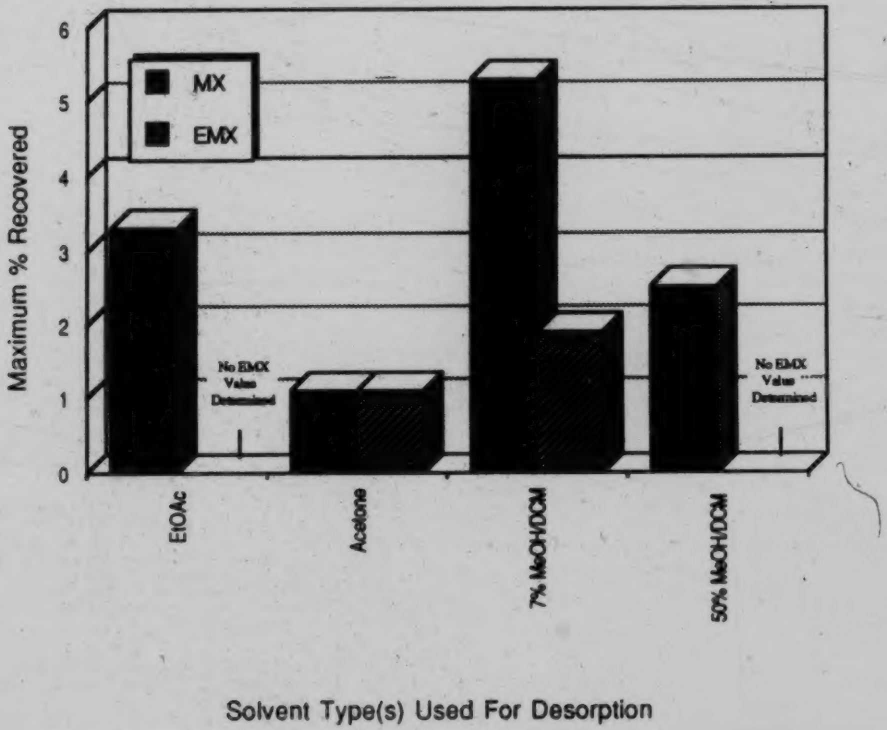


Figure 6.29 Comparison of MX Recovery Efficiencies Using Various Solvent Types and High Temperature Desorption (Expt. AD-89-6)

The decrease in experiment AD-89-6 could possibly be attributable to high temperature decomposition effects. Both EtOAc and 50% MeOH:DCM removed similar albeit lower amounts of MX. This observation is consistent with results from experiment AD-89-5 for the same solvents. Acetone continued to provide low recoveries. In summary, there appeared to be no advantage to increasing the equilibration temperature during desorption.

6.5.8 Summary

To illustrate that an adsorption mechanism was involved in the removal of MX and EMX from water using activated carbon, various combinations of solvents and desorption conditions were examined in attempts to recover MX and EMX from activated carbon.

Table 6.30 lists the amounts of MX and EMX recovered from the carbon after each of two successive desorption steps using ethyl acetate. While the overall recoveries were low, the data clearly show that at least some of the removal capacity of Filtrasorb 400® for MX and EMX is adsorptive, rather than due to irreversible chemical reaction.

Recoveries of both MX and EMX from the carbon were generally greater (in the case of MX, much greater) after the second extraction with ethyl acetate. These values were higher than would be expected from simple isomerization of EMX to MX at the acidic pH utilized during the desorption step and thereby support an adsorption/desorption mechanism. Also as expected, the greatest amount of MX and EMX was recovered from the solutions containing the least amount of carbon (highest surface loadings). Consequently,

Table 6.30 MX and EMX Recovered from Activated Carbon Using Successive Desorption with Ethyl Acetate

Weight of Carbon (mg)	Mass Recovered (ng) 1st extraction (150 mL EtOAc)	Mass Recovered (ng) 2nd extraction (300 mL EtOAc)	Overall Percentage Recovery (%)
MX			
13.0	94	878	1.8
19.2	66	690	1.2
29.7	66	212	0.5
EMX			
13.0	18	58	0.8
19.2	22	35	0.6
29.7	19	43	0.6

Selected data from experiment AD-88-1

Initial mass of MX on carbon =70,700 ng
Initial mass of EMX on carbon=29,700 ng

desorption experiments employed the smallest practical carbon dosage possible, nominally 10 mg.

As shown in Table 6.31, each of the solvent systems investigated without displacer produced similar MX recoveries, ranging between 4.5% and 6.7% (Expt. AD-88-3). Of these, ethyl acetate gave the highest recovery at 6.7%. Except for the first experiment, less EMX was recovered on successive solvent extractions regardless of the solvent system used or whether a displacer was present. The overall percentage recovery of EMX was only about half of that for MX. Since 10% of the solution volume was acidified to pH ≤ 2, some isomerization of EMX to MX would be expected to occur during the desorption steps (Kronberg and Vartiainen, 1987). However it is also possible that different mechanisms govern the adsorption and possible reaction of MX and EMX with carbon.

The presence of a displacer did not improve recoveries (for 1 day desorptions), regardless of its concentration (Table 6.31). Experiment AD-89-5, a solvent system consisting of displacer in 7% methanol in dichloromethane attempted to directly reproduce the solvent conditions reported elsewhere (Thakkar and Manes, 1988). In spite of the fact that the resulting solution was not homogeneous, this system produced the highest MX recoveries (5.8%) of those employing displacer compound and a one day desorption period. However, further support for a removal mechanism which is at least partly adsorptive was obtained in that a second desorption using a 50% methanol in dichloromethane solution containing displacer produced a higher MX recovery (10.7%) when desorbed for 2

Table 6.31 MX and EMX^a Recovered from Activated Carbon for Various Desorption Solvent and Displacer Conditions

Solvent	EXPT. AD-88-1		EXPT. AD-88-3	EXPT. AD-88-4	EXPT. AD-89-5		EXPT. AD-89-6
	(1d. desorb.)	(2.8d. desorb.)	(1d. desorb.)	(1d. desorb.)	(1d. desorb.)	(2d. desorb.)	(1d. desorb)
	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery
Ethyl Acetate	0.1/0.2	1.6/0.6	6.7/NVD	0.6/3.7	2.2/1.2	-	3.3/NVD
Acetone	-	-	4.5/NVD	1.1/3.3	0.6/1.2	-	1.1/1.1
7% MeOH/DCM	-	-	-	-	5.8/1.1	-	5.3/1.8
50% MeOH/DCM	-	-	1.9	5.0/NVD	2.4/1.4	10.7/1.4	2.5/NVD

(a) MX/EMX based on maximum recovered values

Adsorption Conditions:
Nominal PGAC dose=10 mg
Sample bottle volume=0.160 L
pH=6.0

Desorption Conditions:
Solvent system volume=0.025 L-0.100 L
pH=2.0

- : Not analyzed
NVD: No value determined

EXPT. 1. Initial spike conc. MX=690 µg/L EMX=310 µg/L
EXPT. 3. Initial spike conc. MX=20,000 µg/L
EXPT. 4. Initial spike conc. MX=20,000 µg/L + 1.5 g benz[a]anthracene-7,12-dione
EXPT. 5. Initial spike conc. MX=10,000 µg/L + 5 mg benz[a]anthracene-7,12-dione
EXPT. 6. Initial spike conc. MX=100,000 µg/L

For Expt. 3-6 the spike contained; MX:96.9%
EMX:3.1%

days as opposed to 2.4% for a 1 day desorption. For the solvent acetone, and a mixture of 50% dichloromethane in methanol, including a displacer resulted in recovery values which were lower than obtained with solvent alone (Expt. AD-88-3). At present no explanation can be offered for the effect of the displacer, although precipitation of displacer during solvent evaporation may have occluded some MX or removed it by adsorption onto the precipitate.

Although typically less than 10% of the adsorbed MX or EMX were recovered in any of the experiments, no compounds were detected which could account for any significant portion of the recovered material. Therefore it is likely that the vast majority of the adsorbed, and perhaps transformed MX and EMX could not be removed from the carbon by the extraction procedures used. It is also possible, however that most of the adsorbed MX and EMX were transformed to compounds which were not detectable by the analytical procedures used. The second alternative is considered less likely since it would be possible, but not probable that transformation fragments would be largely unextractable, underivatizable or ECD-insensitive. Therefore, assuming that transformation was a predominant removal mechanism, the presence of GD/ECD peaks representing these products would be expected following desorption experiments.

7.0 CONCLUSIONS

The following conclusions may be drawn fron this study involving removal of trihalomethanes and MX using activated carbon:

7.1 Removal of THM's by Activated Carbon

1. For chloroform removal in GAC contactors, a very good agreement was obtained using the Equilibrium Column Model (ECM) between the predicted number of bed volumes fed (BVF) to breakthrough and the midpoint in actual breakthrough curves. This agreement was obtained when the model incorporated Freundlich parameters adjusted to account for capacity reduction due to pre-loading by "background organics" and (unavoidably) some THMs. This agreement was verified for two different carbons and two operating seasons. The overshoot concentration as observed for chloroform in 1986 immediately prior to full-scale contactor shutdown also agreed well with ECM predictions either with or without the presence of Hypothetical Components (HC's).
2. Isotherm experiments designed to evaluate the effect of pre-loading carbon with background organics for varying lengths of time showed that a reduction in the Freundlich K parameter occurs as a function of pre-loading time. (For experimental reasons the pre-loading unavoidably included adsorption of THMs along with the background organics.) A large decrease in the adsorptive capacity for chloroform and bromodichloromethane was observed during the first 8 weeks

of pre-loading. This observation substantiates previous Buffalo Pound full-scale data, suggesting that the reduction in lower bed capacity for trihalomethanes may be largely due to blockage of adsorption sites by pre-adsorbed background organics.

3. Ideal adsorbed solution theory (IAST) allowed competitive adsorption effects to be accurately predicted for individual trihalomethane components in mixtures of known composition. Typically, the model successfully predicted adsorption in the 10 μg/L to 100 μg/L equilibrium concentration range, representing conditions experienced at the Buffalo Pound water treatment plant. IAST however was also found useful in predicting equilibrium concentrations as low as 2 μg/L and as high as 500 μg/L.

4. Hypothetical components (HC's) were used successfully in conjunction with IAST to represent competition in both known and unknown mixtures. The unknown mixtures were actual Buffalo Pound GAC influent water collected during the full-scale contactor operating period. In this case the HC's represented the competition due to simultaneous or co-adsorption of background organics, as opposed to the longer term pre-loading effect. HC's were obtained by fitting Freundlich parameters to bromodichloromethane, a weakly adsorbing tracer compound singled out of the background matrix.

5. Averaged HC parameter values determined for four different water matrices were used successfully to represent the

background adsorptive strength during the GAC contactor operating period. This result suggests that changes in the background matrix are small and would not significantly influence IAST predictions concerning specific compound adsorption during actual full-scale GAC operation.

6. A sensititivy analysis conducted on individual HC parameter values (K, 1/n, and C_0) showed that changes in initial estimates of C_0 and K up to 50% will not significantly influence adsorptive capacity predictions. For the Buffalo Pound water treatment plant, capacity predictions for the summer operating period could therefore likely be predicted based on a single isotherm analysis for each compound of interest and carbon. The isotherm would be performed with actual GAC influent water, spiked with the compound of interest if necessary. However, as shown in Section 7.6, for predictions with the ECM the effect of co-adsorption of background organics is much less significant than that of pre-loading.

7. Preliminary investigations have shown that reduction in adsorptive capacity for a specific compound attributable to pre-loading may be estimated by measuring TOX adsorbed on the pre-loaded carbon. Therefore, for a given compound it may be possible to relate residual adsorptive capacity to pre-adsorbed TOX, once a relationship has been established.

7.2 Removal of MX by Activated Carbon

1. The strongly mutagenic compound MX was found to be very well removed from water by activated carbon over a wide concentration range. Isotherm experiments conducted at pH 6 and 20°C produced Freundlich K and 1/n values of 12,400 µg/g and 0.21, respectively, for the removal of MX on virgin Filtrasorb 400® activated carbon, assuming adsorption as the removal mechanism. Because of MX instability at high pH values, the conditions chosen represent the low end of drinking water treatment practice. These results show MX to be very strongly adsorbed when compared to compounds such as trihalomethanes which might be considered for removal from water using GAC. Using a typical contactor operating flowrate and chloroform influent concentration, and assuming a relatively high influent concentration for MX (0.1 µg/L), breakthrough for chloroform would occur approximately 11 to 64 times earlier than for MX, depending on pre-loading conditions.

2. At an equilibrium concentration of 1 µg/L, a reduction of 40% was observed in the capacity of GAC for MX following 10 weeks of pre-loading with natural organic matter. A change in isotherm slope from 0.21 to 0.50 also indicated that MX removal to low levels would require higher carbon dosages than suggested by pure-water isotherms. The shift in slope could also, reflect a change in removal mechanism (adsorptive vs reactive) on the pre-loaded carbon due the presence of

material that MX could react with, although this could not be established within the context of this research.

7.3 Occurrence of MX in Water Treatment Plants

1. In a survey of six water treatment plants, MX was found in two pre-chlorinated raw waters and one laboratory-chlorinated raw water. MX was also present in one post-chlorinated finished water. EMX was present in various samples, with no apparent correlation with the presence of MX.
2. For some of the plants examined, MX concentrations appeared to be correlated with TOC and TOX values. However, two plants with very high TOC concentrations showed non-detectable MX levels, suggesting that MX formation might be related to the type of organic matter present.
3. One plant which used GAC appeared to be capable of removing MX precursors during treatment.

7.4 Recovery of MX From Activated Carbon

Investigations involving solvent extraction of MX from activated carbon show that at least some of the removal of MX and its isomer EMX is attributable to adsorption, although some reaction to small amounts of other compounds does occur. Three of these compounds have been identified, however their mutagenic properties are unknown.

8.0 RECOMMENDATIONS

8.1 GAC Treatment Practice

The following recommendations with respect to GAC treatment practice can be made on the basis of this study:

1. The results of computer models requiring relatively simple input data (i.e. Equilibrium Column Model) can be useful as a tool to provide an approximation of the breakthrough order and timing of the midpoint of the breakthrough curve for specific compounds, in the design of both pilot and full-scale GAC contactors. When applied these models should incorporate input capacity data based on experiments which assess the impact of pre-loading with background organics. This is especially important in cases where relatively high TOC concentrations are present.
2. In cases where only isotherm data are used for the design of either pilot or full-scale GAC contactors, experiments should be conducted in sufficient detail to allow the effect of co-adsorption of background organics to be addressed.

8.2 Further Studies

The present study has revealed three areas of significant interest which should be considered for more detailed investigation:

1. More sophisticated computer models which include mass transfer resistance should be applied to predict breakthrough

of THMs at Buffalo Pound. These models should incorporate capacity reductions attributable to pre-loading, as well as the effect of backwashing. Results should then be compared to those of the simpler models to determine the extent of sophistication required to provide adequate performance estimates. Once successful application has been demonstrated at Buffalo Pound, the models may be used in other locations considering GAC treatment.

2. Further research should be directed towards identifying specific organic precursors and chlorine dosages required for the formation of MX and EMX in water treatment.
3. The possible reaction of MX and EMX with carbon surfaces should be evaluated for various types of virgin carbon and carbon which has remained in service for extended periods of time. Once specific reaction products are determined they should be evaluated on the basis of their individual adsorbabilities by GAC, mutagenic potentials, and relationship to specific types of organic precursors.
4. Detailed extraction methods should be developed which quantitatively describe the recovery of MX and EMX from activated carbon. The use of ^{13}C labelled MX and EMX in combination with gas chromatographic/mass spectrometric analysis would be useful for this purpose.
5. The type of procedure used to pre-load carbon should be assessed to define a method which most easily and accurately reflects pilot and full-scale operating characteristics.

6. The methodology used to prepare pre-loaded carbon for isotherm experiments should be considered in detail. Emphasis should be placed on defining a drying, crushing, and sieving procedure which minimizes the loss of organics present on the carbon.

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Appendix I

Activated Carbon Preparation and Analyses Methods

Appendix I.1 Apparent Density Methodology

1. Apparatus

Specific details concerning the testing apparatus are described elswhere (AWWA,1974). Reservoir and feed funnels are glass or metal. The metal vibrator is 26-guage galvanized sheet metal. A balance having a sensitivity of 0.1 g is required.

2. Procedure

(a) Carefully place a representative sample of the carbon into the reservoir funnel. If the material prematurely flows into the graduated cylinder, return the material to the reservoir funnel.

(b) Add the sample to the cylinder using the vibrator feeder at a uniform rate not less than 0.75 mL/s nor greater than 1.0 mL/s up to the 100 mL mark. Adjust the rate by changing the slope of the metal vibrator or raising or lowering the reservoir funnel, or both, or by using a variable autotransformer to vary the current to the buzzer transformer.

(c) Transfer the contents from the cylinder to a balance pan and weigh to the nearest 0.1 g.

2.1 Apparent Density Test Procedure Modification

The procedure used in determining the apparent density of granular activated carbon was as specified by the AWWA (1974), with one modification. The AWWA (1974) standard specifies that a sample volume of 100 mL should be used. Due to a lack of sufficient quantities of carbon, some samples were tested using a 50 mL volume. Prior tests had shown that volumes of either 50 mL or 100 mL yield the same apparent density.

3. Moisture Content Determination

(a) Place a known mass of carbon in a watchglass

(b) Dry the carbon overnight at 105°C

(c) Reweigh the sample after drying, and determine the mass of solids.

The moisture content (w) is calculated as:

$$w = \frac{M_w}{M_s} \times 100\ (\%)$$

where M_w = mass of water
M_s = mass of solids

4. Calculation

Calculate the apparent density in grams/milliliter on a dry basis as follows:

$$\text{App. density} = (\text{Weight of Carbon}) \times \frac{(100 - \text{Percentage Moisture})}{100 \times (\text{Sample Volume, mL})}$$

Appendix I.2 Particle Size Distribution Method and Results

U.S. standard mesh sieves numbers 8, 10, 12, 18, 20, 25, 30 and 40 were used, along with a Roto-tap® shaker to separate the carbon into various size ranges. The sieves were weighed and placed on the Roto-tap in order of increasing fineness, with a pan placed on the bottom beneath the finest sieve. Approximately 130g of GAC was placed in the top sieve of the stack. The sieve stack was then placed on the Roto-tap and the timer set for 3 minutes. After the sample was shaken the sieves were removed from the Roto-tap. Starting with the #8 sieve and working down the stack, the pre-tarred sieves were weighed using a Mettler balance accurate to 0.01g. After each sieve was removed from the stack and emptied it was placed back on the stack and gently brushed with a wire brush to free any particles that may have been trapped in the mesh. A check was conducted on the accuracy of the analysis. If the total amount retained varied by more than ±2% from the total initial amount of GAC the analysis was rejected.

Sieve analyses results are presented in Figures I.2.1 to I.2.5. The unwashed sieve plots represented carbon grain size as received and served as a check on manufacturer specifications. Size distribution plots obtained after washing represent the carbon as it would occur in column operations, following an initial backwash to remove fines. This sieve analysis also represented the grain size distribution prior to crushing the carbon for isotherm studies.

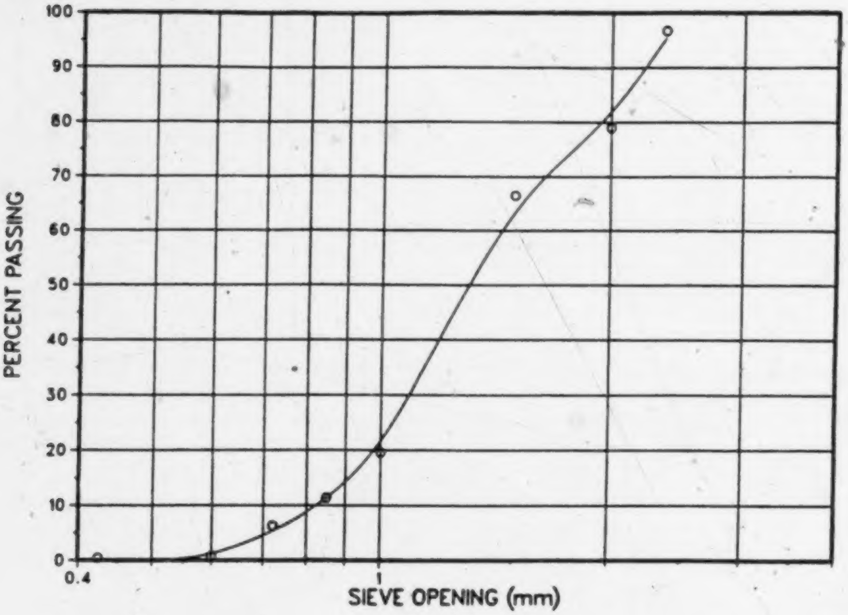

Figure I.2.1 Ceca 830 Unwashed Particle Size Distribution

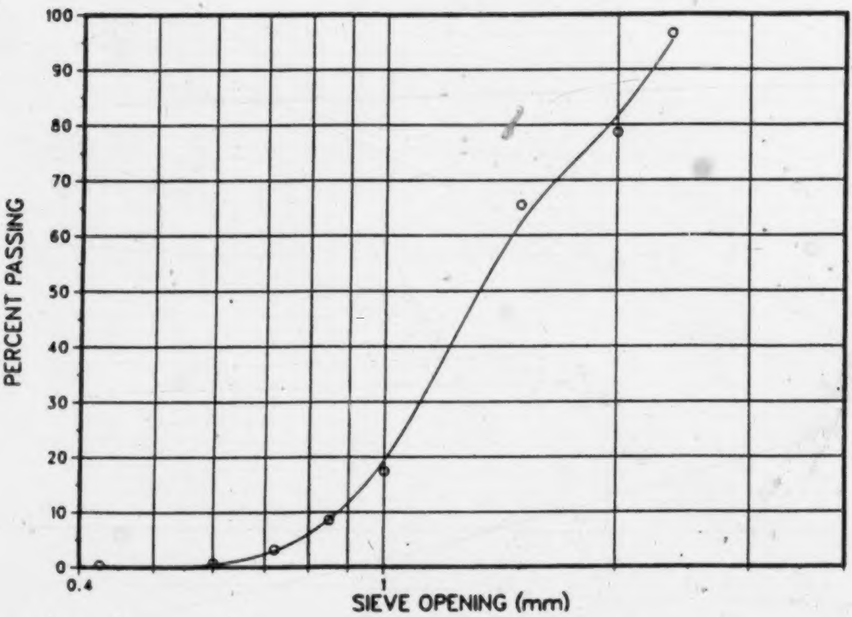

Figure I.2.2 Ceca 830 Washed Particle Size Distribution

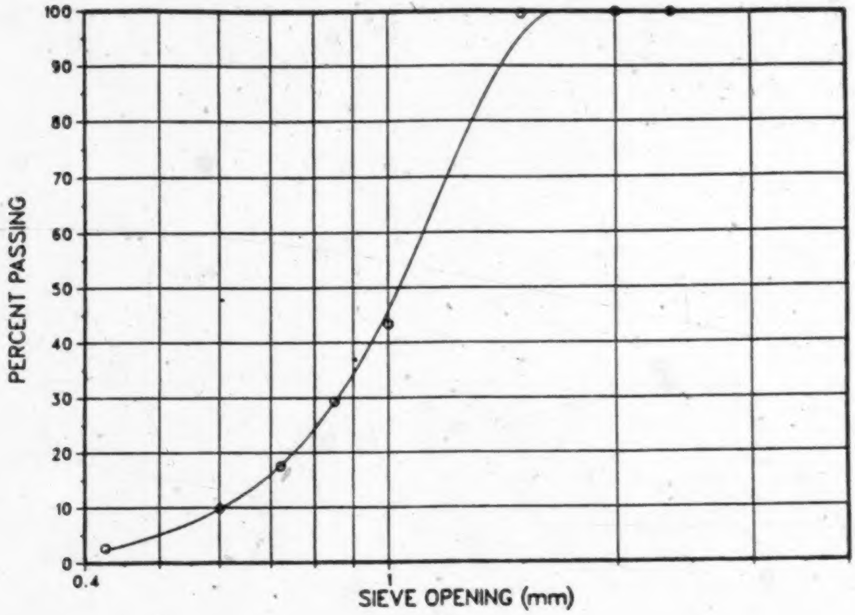

Figure I.2.3 Filtrasorb 400® Unwashed Particle Size Distribution

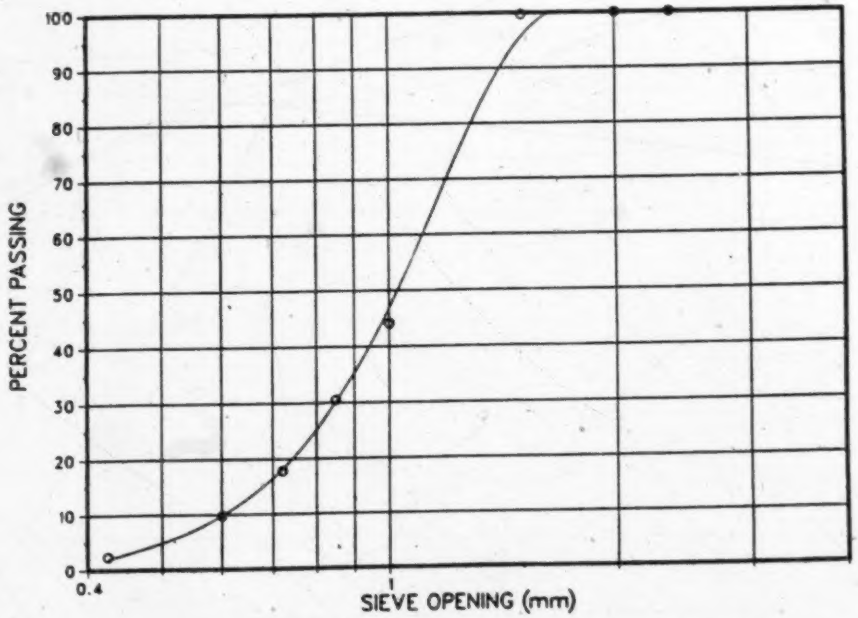

Figure I.2.4 Filtrasorb 400® Washed Particle Size Distribution

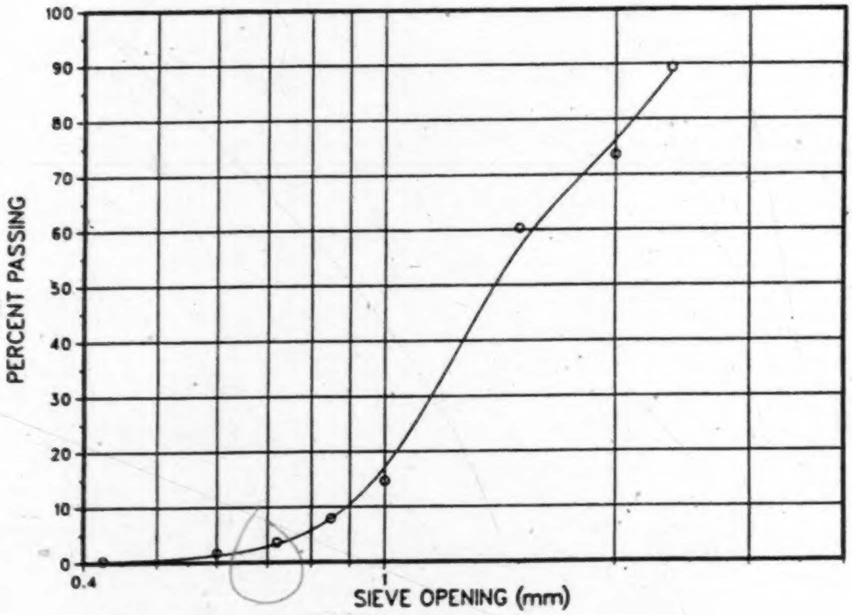

Figure I.2.5 Filtrasorb 300® Unwashed Particle Size Distribution

Appendix I.3 Preparation of GAC for Isotherm Studies

The following procedures were adapted from those provided by Dr. J. C. Crittenden and are used at the Michigan Technological University.

All equipment that was to come into contact with the GAC was cleaned using the procedures outlined below:

(a) All glass, Teflon®, and stainless steel utensils were washed in a dishwasher with sparkleen, a phosphate free laboratory detergent.

(b) All of the equipment was then rinsed several times with organic free water in order to remove unwanted organics.

(c) All glassware, teflon®, and stainless steel was placed in a drying oven at 65°C until dry.

1. GAC Splitting

Due to the settling and stratification properties of GAC in bulk containers, it is necessary to obtain a representative sample from the total volume of GAC. This was obtained by splitting the original container into progressively smaller volumes until the required volume of GAC is achieved. Starting with a 25 kg bag of GAC, the following procedure was followed until the volume of GAC was reduced to 4 L.

(a) A riffle splitter was set up with 2 stainless steel pans, labelled A and B, to receive the carbon.

(b) Approximately 1000 mL aliquots of GAC was removed from the bulk 25 kg container and passed through the riffle splitter.

(c) The GAC retained in tray "A" was poured into a bag likewise labelled "A".

(d) The GAC retained in tray "B" was poured into a bag labelled "B".

(e) When the original container was emptied bag B was set aside for storage and the GAC contained in bag A was passed through the above procedure once again.

When the quantity of GAC contained in bag "A" was reduced to approximately 4 L, the carbon was removed from the bag and placed into 4 teflon® capped 1 L borosillicate jars for storage.

2. GAC Washing

After splitting, the GAC was washed according to the following procedure. This was done to remove any carbon fines that may have been present in the sample.

(a) Approximately 200 mL of GAC was placed in a 1 L beaker. Organic-free (Milli-Q®) water was then poured into the beaker and the contents were agitated causing the fines to be suspended in solution. The water was then poured off the top of the beaker through a buchner funnel taking care to minimize GAC losses. This procedure was repeated 3 times.

(b) The washed carbon was then placed in thin layers (1.0 cm) on evaporating dishes and the dishes were placed into a 103°C oven until the GAC was dry (~ 16 hrs.).

(c) When dry, the GAC was removed from the oven and placed in a large dessicator until cool, then stored in a teflon® capped bottle.

3. Crushing of GAC

To reduce the original GAC to the required particle size for isotherm studies, it was necessary to design and optimize a crushing procedure. Initially 10g of GAC was placed in a stainless steel crushing container. Different numbers of balls, and combinations of ball sizes, as well as crushing times were utilized to optimize the percentage of the original sample retained in the 200 x 400 mesh size range. It was determined that 64 chrome-plated 0.64 cm diameter steel balls and a crushing time of 2 minutes in the SPEX® mixer/mill yielded the best results, with approximately 80% of the powdered GAC retained in the desired range. Appendix I.5 contains complete details regarding the crushing optimization procedure.

4. Washing of Powdered GAC (PGAC)

Once the GAC has been crushed, it was necessary to wash it to remove any extremely fine material. Approximately 60g of the PGAC was placed in a polycarbonate centrifuge tube. The centrifuge tube was then filled to within 2.5 cm of the top with organic free (Milli-Q®) water, sealed, and shaken. The tubes were placed in a Sorvall® GS-3 head, mounted in a Sorvall® RC-5B centrifuge, and centrifuged at 2300 rpm for 30 minutes. The supernatant was poured off and the resulting slurry placed into ceramic evaporating dishes. The evaporating dishes were placed in an oven at 103°C until the PGAC was dried then placed in a dessicator to allow the PGAC to cool.

Appendix I.4 Procedure for Freeze-Drying Granular Activated Carbon

Activated carbon samples were prepared for freeze-drying using the following procedure:

(1) Two 250 mL round bottom flasks were washed, rinsed with organic-free water, and baked (65°C) for at least one hour.

(2) Approximately 25 g of carbon was weighed into a beaker, and enough organic-free water was added to form a slurry.

(3) Dry ice was placed in a flat bottom pan, and methanol was added to a depth of approximately 3 cm.

(4) The 25 g slurry of GAC was transferred into a labelled round bottom flask.

(5) Each flask was covered with a nylon mesh which would permit vapour passage but retain any carbon fines within the flask.

(6) The flasks were rotated by hand for 2 to 3 minutes in a dry ice slurry, attempting to evenly spread the carbon about the lower two-thirds of the flask sides. The spinning motion was continued until all GAC was frozen in place.

(7) When all flasks were prepared, they were placed on cork rings in a vacuum chamber. The freeze-drier condensor was pre-cooled to -60°C. The chamber was sealed, and the vacuum started, evacuating the chamber to a pressure of 10 microns of mercury.

(8) The GAC was left in the freeze-dryer for approximately 24 hours to ensure the sample was completely dry. It was then removed from the flasks and stored in labelled 118 mL amber

Quorpak bottles equipped with screw caps and teflon® liners (Fisher Scientific, Ottawa, Ontario, Canada).

Appendix I.5 GAC Crushing Optimization Procedure

Using a SPEX® 2000 Mixer/Mill, and the manufacturers recommendation of (4) 1/4" and (2) 3/8" diameter stainless steel balls, initial runs were made using crushing times varying from 30 seconds to 7 minutes. In all cases, less than 20% of the crushed carbon was retained within the desired size range. The majority of the carbon was either not crushed, or crushed too finely. The two 3/8" diameter balls were removed from the mill, as it was suspected that these might have been the major reason why the carbon was being crushed into very fine particles.

Two runs were made using (4) 1/4" balls. The results were better, with 48% being retained following 10 minutes crushing time. However, the majority of the sample passed through the #400 sieve at both 70 seconds and 10 minutes. Typical carbon crushing standards (USEPA, 1973) recommend that (64) 1/4" balls be used in the mill. For this reason, (64) 1/4" chrome-plated balls were obtained. At a crushing time of 2 minutes, approximately 78% of the sample was retained within the desired size range. The final crushing period was thereby determined to be 2 minutes using (64) 1/4" diameter balls.

Appendix I.6 Pre-Loading Column Installation/Operation

1. Testing and Installation

The completed pre-loading column was temporarily installed for initial testing at the Rossdale water treatment plant, Edmonton, Alberta and operated for a period of approximately ten days. Each "boat" was loaded with approximately 15g of pre-washed GAC and the influent flowrate set at 0.34 L/min. These conditions served to represent typical operating conditions at Buffalo Pound. During this trial period no significant operating problems were observed. Upon completion of the trial run the column was dismantled and cleaned.

All components of the pre-loading column including the carbon sample boats, screens, end fittings, and glass column were thoroughly washed and baked in the laboratory. This procedure involved the following steps: i) all components were placed in an acetone bath for a period of three to four hours, ii) all components excluding the glass column were acid washed (phosphoric acid) at 85°C in a laboratory dishwasher and rinsed with distilled water, iii) all components were baked overnight in a drying oven at 65°C, iv) the stainless steel boats were assembled, including screens, placed in the glass column and end caps installed, v) Milli-Q® reagent grade deionized water was allowed to flow through the column for a period of approximately 2 hours, and vi) the column was disassembled and all components oven-dried at 65°C.

The pre-loading column was shipped to Buffalo Pound and installed on February 19,1987 as shown in Figure I.6.1. Actual operation commenced February 19, 1987.

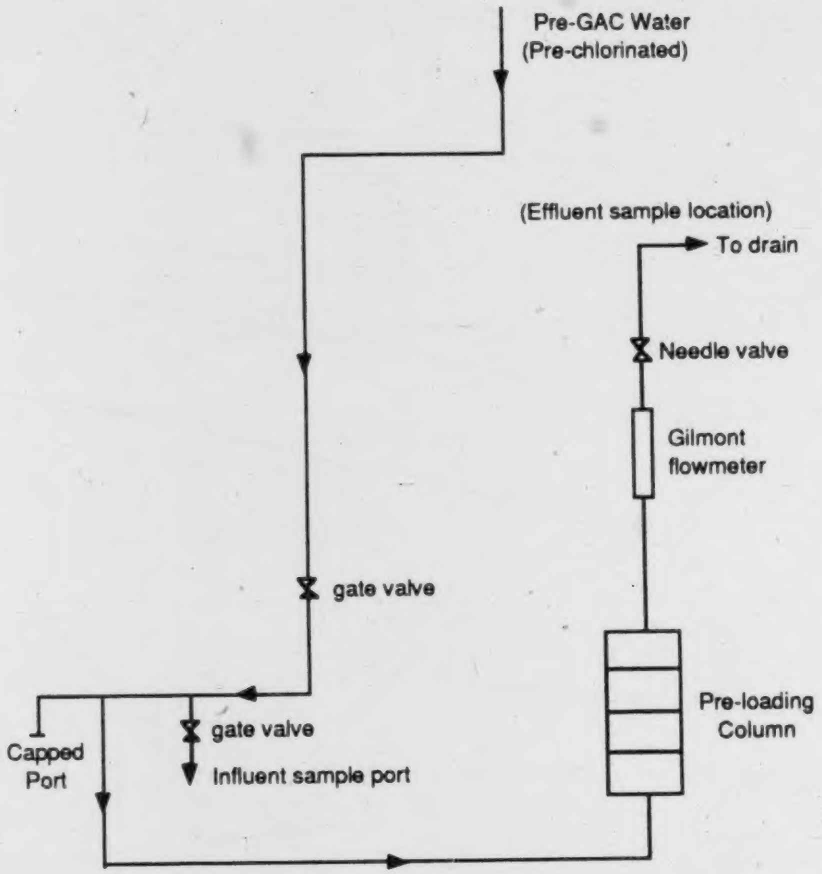
Pre-GAC Water
(Pre-chlorinated)
(Effluent sample location)
To drain
Needle valve
Gilmont
flowmeter
gate valve
Pre-loading
Column
gate valve
Capped
Port
Influent sample port

Figure I.6.1 Pre-Loading Column Installation Schematic for Buffalo Pound Water Treatment Plant

2. Influent and Effluent Sampling

To provide an estimate of mass loading on the GAC, samples of influent and effluent were collected at the same time. These samples were then analyzed for TOX, THM's and TOC. The difference between influent and effluent liquid phase concentrations was used as an estimate of the TOX, THM's, and TOC adsorbed on the GAC. The samples were always collected on the same day of the week, commencing at start-up and at weekly intervals thereafter. An influent sample was collected immediately upstream of the column using a 1.3 cm gate valve. The effluent was collected immediately downstream of the flowmeter. During weeks when carbon samples were removed from the column, samples were collected immediately before column shutdown. Glass 500 mL bottles equipped with screw caps and teflon® liners were used for both samples. Samples were collected, labelled and preserved as per the following:

Influent	1 sample for TOX and THM analyses 1 sample for TOC analyses
Effluent	1 sample for TOX and THM analyses 1 sample for TOC analyses

Sample preservation:

(a) TOX and THM's - add 1 mL of 0.1M sodium thiosulphate

(b) TOC - add 1 mL nitric acid to acidify to pH 2.

Samples were shipped in wooden boxes each containing four 1L bottles, to the University of Alberta Environmental Laboratory every two weeks. Prior to and after shipment the samples were stored at 4°C.

Appendix I.7 GAC Centrifugation Optimization Methodology

To determine the required centrifuge operating parameters for removal of powdered activated carbon from solution following completion of an isotherm experiment the variables of rotational speed and time were evaluated on the basis of minimizing turbidity in extracted samples. Analyses were performed by C. Rutledge, Women in Scholarship, Engineering and Technology student.

The 160 mL serum bottles in use for isotherm experiments were not designed for the centrifugation, therefore the rotational speed was limited to a maximum of 1800 rpm. The remaining parameter to be optimized was centrifugation time.

By varying the carbon dosage over the anticipated range of 0 to 60 mg, and centrifuging for time periods of 5, 10, 15, 20, and 30 minutes, a plot comparing turbidity to carbon dosage was generated (Figure I.7.1). At times less than 30 minutes, a direct correlation was found to exist between the carbon dose and turbidity. At a centrifuge time of 30 minutes however, the turbidity was essentially constant, regardless of the carbon dose.

Using this criteria, the centrifuge parameters were set at a rotational speed of 1800 rpm for 30 minutes.

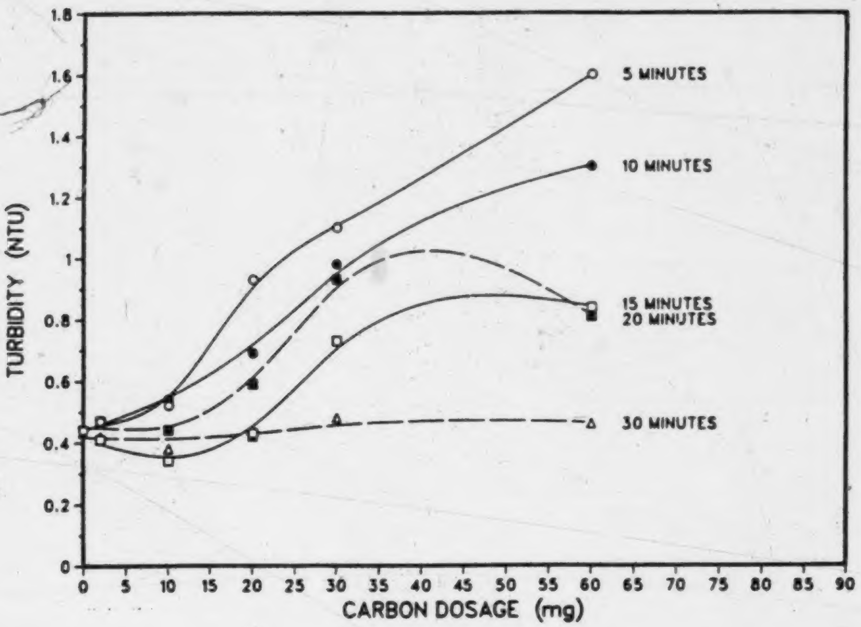

Figure I.7.1 Centrifuge Time Optimization For F-300 Carbon, 325-400 Mesh

Appendix II

Gas Chromatography Operating, Calibration and Quality Control Data For THM Analyses

1. Instrument Operating Parameters

Table II.1 Instrument Operating Parameters for USEPA Method 501.1

Purge and Trap Sampler: Tekmar® LSC-2 with Model ALS autosampler

Purge - 11 min
Desorb - 4 min
Bake - 10 min
Transfer Lines - 140°C
Purge Gas - Nitrogen at 40 mL/min
Purge Volume - 5 mL
Trap Material - Tenax® GC

LSC-2 Set Points:
  SP1 (Trap) - 30C
  SP2 (Column Temp at start of GC run) - 61°C
  SP3 (Trap Preheat) - 100°C
  SP4 (Desorb Temp) - 180°C
  SP5 (Trap Bake Temp) - 225°C

Gas Chromatograph: Hewlett Packard® Model 5790A or Varian® Model 3300

Column: - 1% SP-1000 on Carbopack® B (60/80 mesh)
  - 3m x 0.25cm

GC Temp: Injection Port - 150°C
  Column - Hold at 60°C for 0.5 min; increase at 8°C/min to 220°C; hold at 220°C for 5 min.
  Detector - 300°C

Carrier Gas: Nitrogen 30 mL/min: 3 mL/min to injector
  27 mL/min directly to column

Detector: Flame ionization
  Hydrogen flow: 30 mL/min
  Air flow: 240 mL/min

Integrator:Hewlett Packard® Model 3390A or Spectra-Physics® Model SP4290

Table II.2 GC Clean-Out Procedure

Fill all tubes with 5 mL organic free water

ALS autosampler:

Purge Time - 05 min - if previous sample concentration < 200 ppb
- 10 min - if previous sample concentration > 200 ppb

Desorb Time - 00 min

Bake Time - 10 min

SP1 (trap) - 98°C

Purge Gas Flowrate - 40 mL/min N_2

Desorb Ready
Desorb Preheat - Togle @ Auto

Bake Toggle @ Reset

Thermocouple disconnected

GC:

All parameters same as for sample run except:

Oven Temperature - 210°C
Detector Temperature - 350°C

INTEGRATOR: Remote and thermocouple switches set off

After tube #10 has finished, switch bake toggle to Auto, step LSC through to bake, and bake out Tenax column for 10 minutes.

2. GC Calibration Data

The linearity of analysis Method 501.1 (USEPA, 1984) was examined by analyzing a series of replicated trihalomethane standards. Each of seven different standard concentrations was replicated six times. During the conduct of isotherm studies standard calibration concentrations extended over the range used in experiments. All aqueous standards of a given concentration were loaded into the purge tubes within 20 minutes of preparation and analyzed on the same day. Standard calibration curves used during the course of experimentation to obtain response factors are shown in Figures II.1 to II.4.

3 Quality Control Program

In order to ensure that laboratory results were reliable a quality control program was designed. This program was designed to indicate when recalibration was necessary due to a change in the response of the detector, or when other problems, such as leaks had developed.

The USEPA (1979) recommends that each analytical run contain the following quality control checks:

a) one blank
b) one midpoint standard
c) one set of duplicate analysis

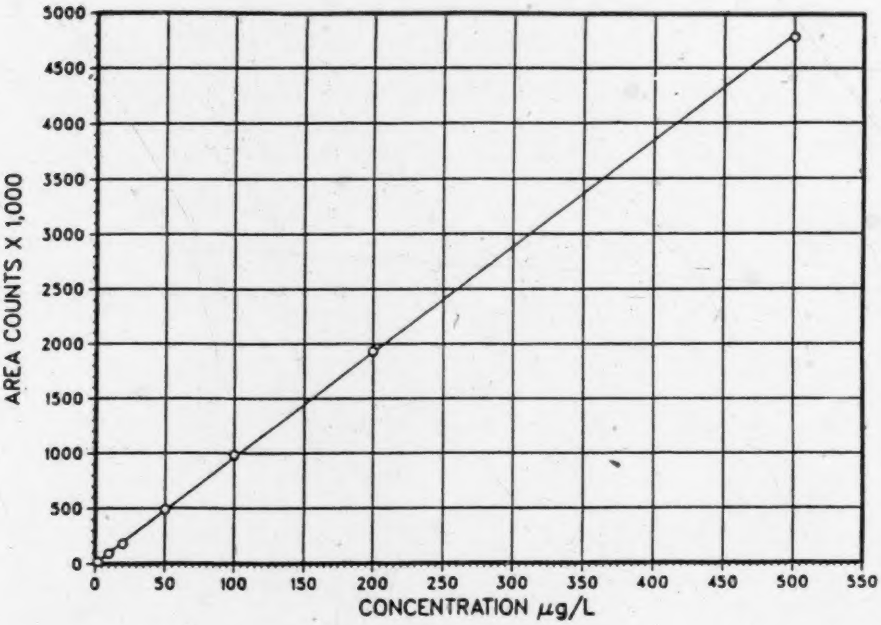

Figure II.1 Chloroform Calibration Curve

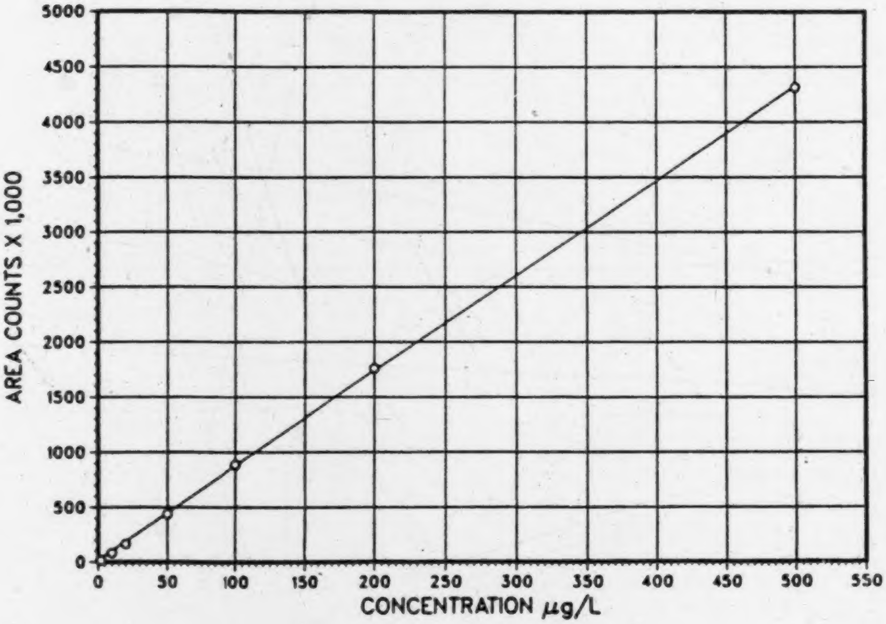

Figure II.2 Bromodichloromethane Calibration Curve

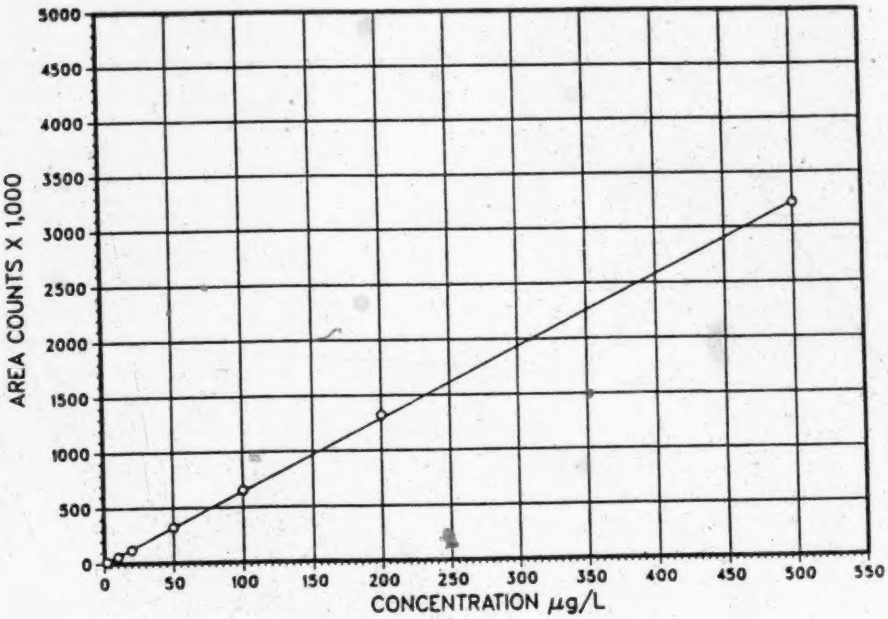

Figure II.3 Dibromochloromethane Calibration Curve

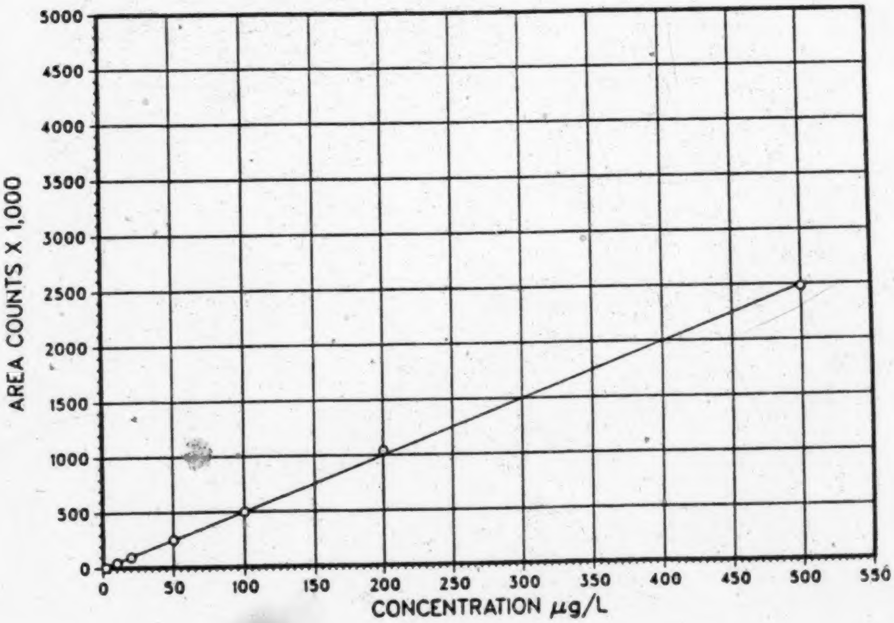

Figure II.4 Bromoform Calibration Curve

Considering the above recommendations, a decision was made such that each sample run would consist of one blank, placed in tube 8, and one 20 ppb standard, placed in tube 9. Although the USEPA (1974) recommends the standard be placed at the midpoint of the run, it was decided that the 20 ppb standard would be placed near the end of the run. In this way, it was possible to determine whether any losses occur in the tube before analysis. The blank was placed immediately preceeding the standard to ensure that no carry over alters the standard. As only two runs, each consisting of 8 samples, a blank, and a 20 ppb standard could be analyzed in a given day, duplicate analysis of one of the samples was not considered due to time constraints.

4. Quality Control Chart Preparation

To ensure that the GC was operating in control, a quality control chart was prepared utilizing data obtained during calibration. A Shewhart chart based upon the percentage recovery of the standard was prepared. The classic Shewhart chart, which is based on the mean and range of the data, is not effective over a large range of concentrations, as the mean and range show a substantial increase as the concentration increases. However, by applying a Shewhart control chart which evaluates the percentage recovery, this problem was resolved and the chart was valid over a broader concentration range (USEPA, 1979).

Utilizing a minimum of 20 samples (APHA, 1985) the area counts from the most recent calibration were tabulated. From the Minitab statistical program utilizing linear least squares, a regression equation relating area counts to concentration was obtained for each trihalomethane component. At the calibration concentrations of 2, 10, 20, 50, 100, 200 and 500 ppb, the regression equation was solved for the area counts for the respective concentration. These calculated area counts were then used as the known values from which the percentage recovery (P_i) for the control standards were calculated.

$$P_i = \frac{\text{Observed Area Counts}}{\text{Known Area Counts}} * 100$$

The average percent recovery ($\overline{P}$) was calculated as:

$$\overline{P} = \frac{1}{n} \sum_{i=1}^{n} P_i$$

The standard deviation for percent recovery (S_p) was:

$$S_p = \frac{\sum_{i=1}^{n} P_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} P_i \right)^2}{n-1}$$

The upper and lower control limits were set at ±3 standard deviations from the mean, and the upper and lower warning limits were set at ±2 standard deviations from the mean (APHA, 1985):

$$UCL = \overline{P} + 3S_p \qquad UWL = \overline{P} + 2S_p$$

$$LCL = \overline{P} - 3S_p \qquad LWL = \overline{P} - 2S_p$$

Once the control chart was completed, the initializing data were checked to ensure that no values exceeded the control limits. Furthermore, assuming the data to be normally distributed, 68 percent should fall within plus or minus one standard deviation of the mean. The control chart was assumed invalid if less than 50 percent of the data falls within this range (USEPA, 1979).

Daily, data from known standards (predominantly 20 ppb) were tabulated and plotted on the control chart. Typical control charts are shown in Figures II.5 to II.8.

An out of control situation as described by the USEPA (1979) is indicated by either:

a) Any point lying beyond the control limits
b) Seven successive points plotting either above or below the mean.

When an out of control situation was identified, analysis were postponed until the problem was rectified.

5. Quantitation Limits

It was necessary to be able to distinguish between actual low concentrations of a specific trihalomethane component and background noise in the detector. During each calibration, a test was run to determine the limits of detection of the gas chromatograph.

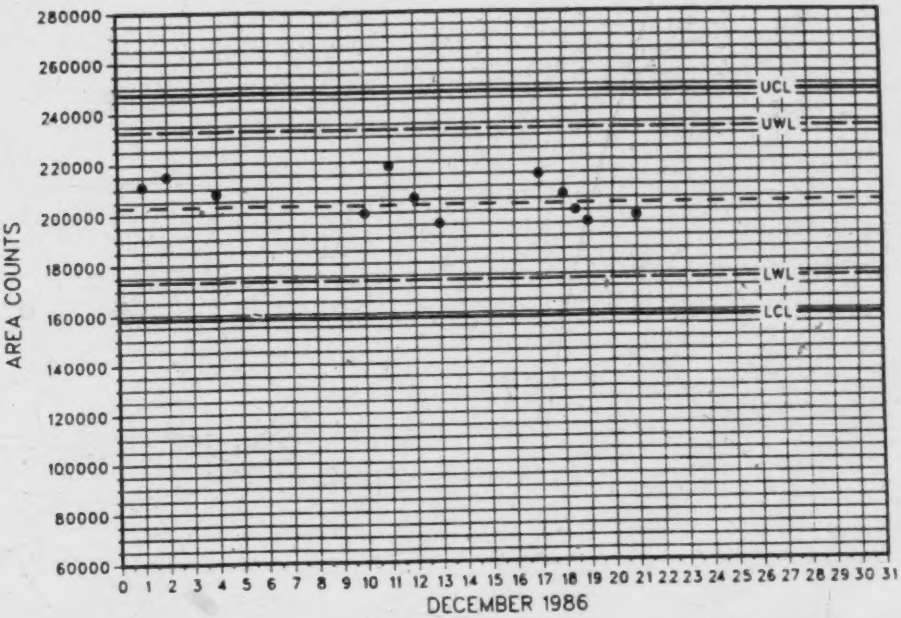

Figure II.5 Chloroform Quality Control Chart

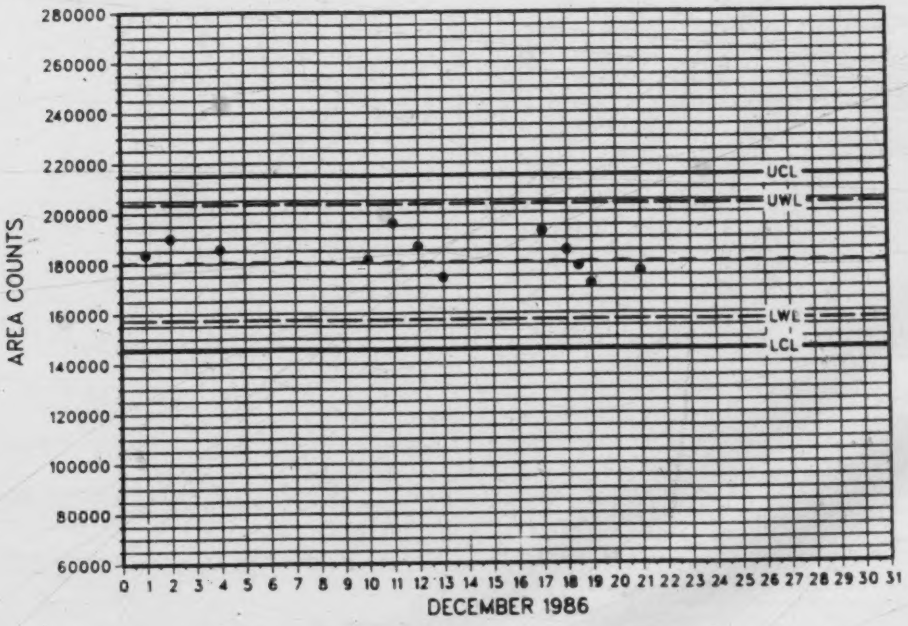

Figure II.6 Bromodichloromethane Quality Control Chart

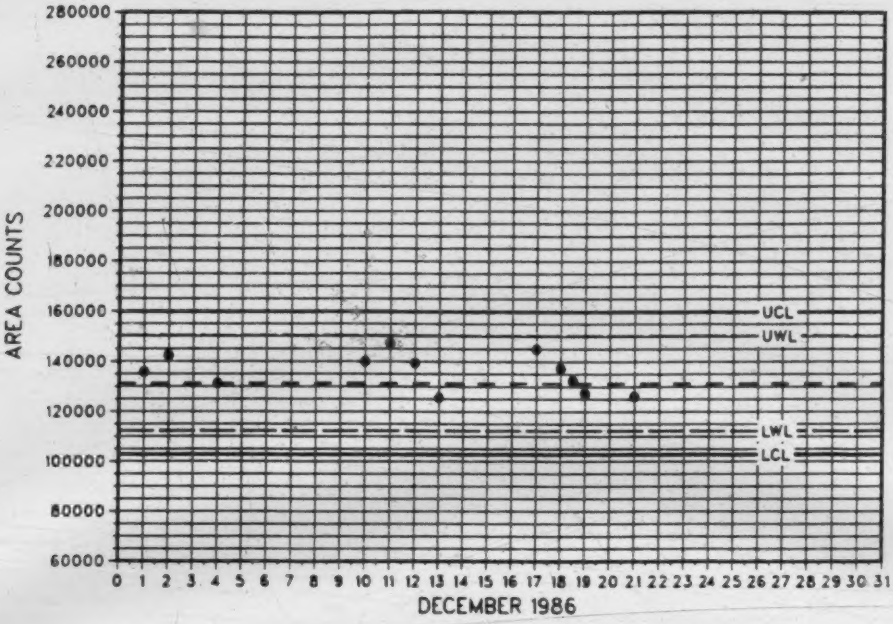

Figure II.7 Dibromochloromethane Quality Control Chart

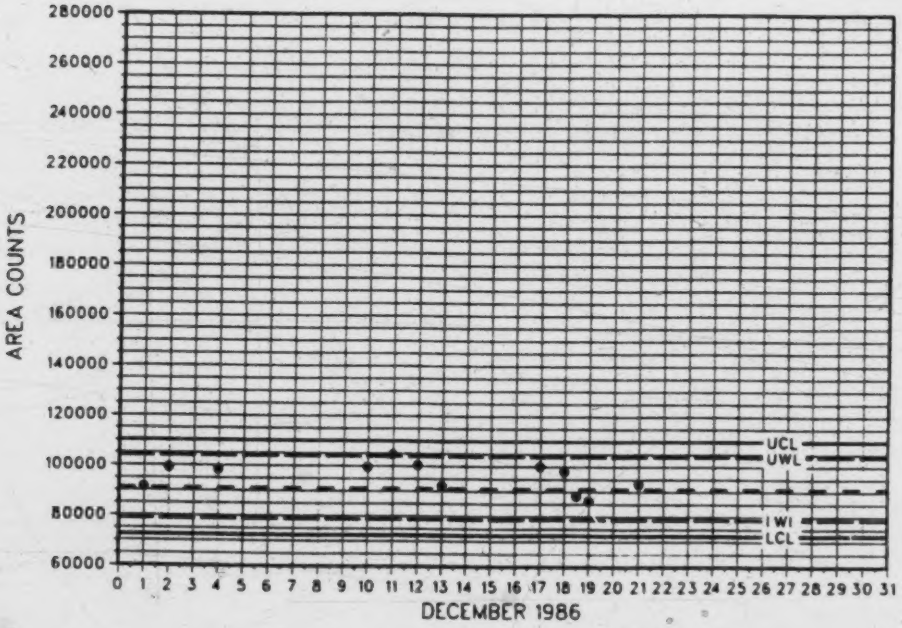

Figure II.8 Bromoform Quality Control Chart

Three sample sets, each consisting of a 2 ppb standard immediately followed by a blank were analyzed, and the limits of detection (LOD) of each set for each trihalomethane were calculated according to a method defined by the USEPA (1984):

$$\mathrm{LOD} = \frac{(A \times \mathrm{ATTN})}{(B \times \mathrm{ATTN})} * (2\ \mu g/L)$$

Where: A = 5 times the noise level or baseline displacement (in mm) at the exact retention time of the trihalomethane.

B = peak height of the 2 ppb standard

ATTN = Attenuation Factor

The mean of the individual detection limits was then calculated and reported as the limit of detection for the given trihalomethane component. Typical detection (quantitation) limits are shown in Table II.3.

Table II.3 Typical Quantitation Limits

All samples; Attenuation 2^-1

		Baseline Displacement (mm)			
Sample		$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
1	blank*	1	1	1	1
	2 ppb STD	35	33.5	21	3.5
	Limit of Detection	0.29	0.30	0.48	0.74
2	blank*	1	1	1	1
	2 ppb STD	34	30	19	13
	Limit of Detection	0.29	0.33	0.53	0.77
3	blank*	1	1	1	1
	2 ppb STD	35	30.5	19	14
	Limit of Detection	0.29	0.33	0.53	0.71
MEAN	Limit of Detection (ug/L)	0.29	0.32	0.51	0.74

* Since baseline displacement was < 1 mm for all compounds, a value of 1 mm was assumed for use in calculations.

Appendix III

Single Solute Isotherms

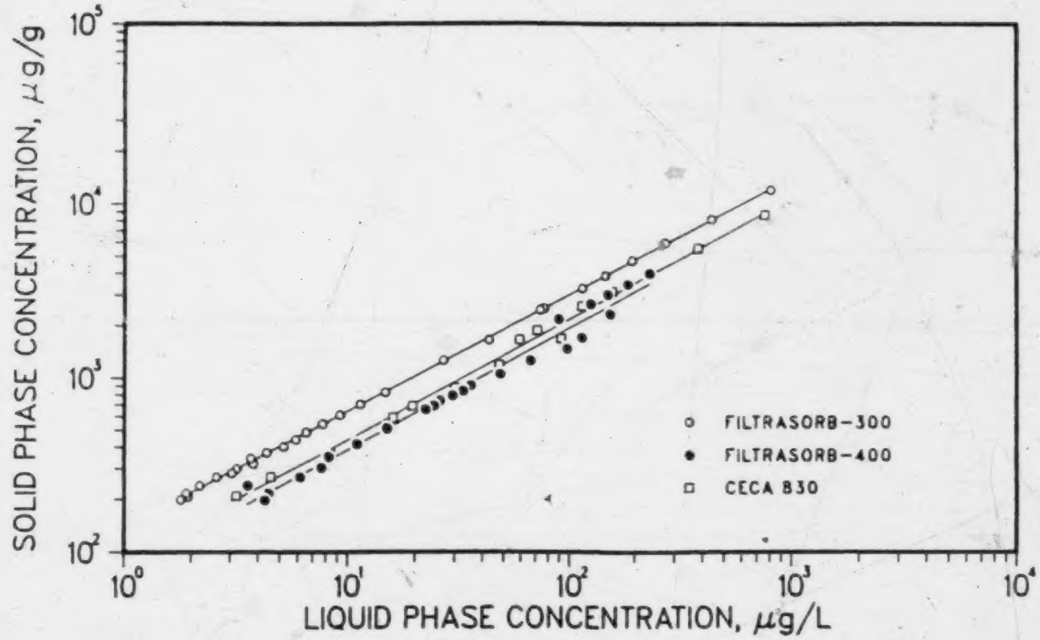

Figure III.1 Comparison of Chloroform Isotherms on F-300, Ceca 830 and F-400 Carbon

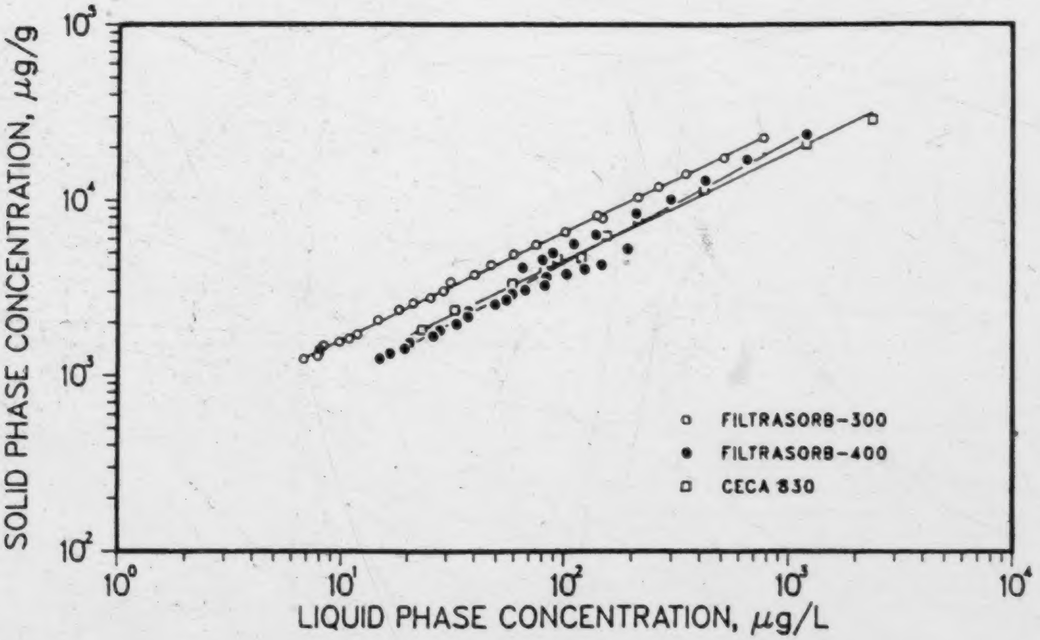

Figure III.2 Comparison of Bromodichloromethane Isotherms on F-300, Ceca 830 and F-400 Carbon

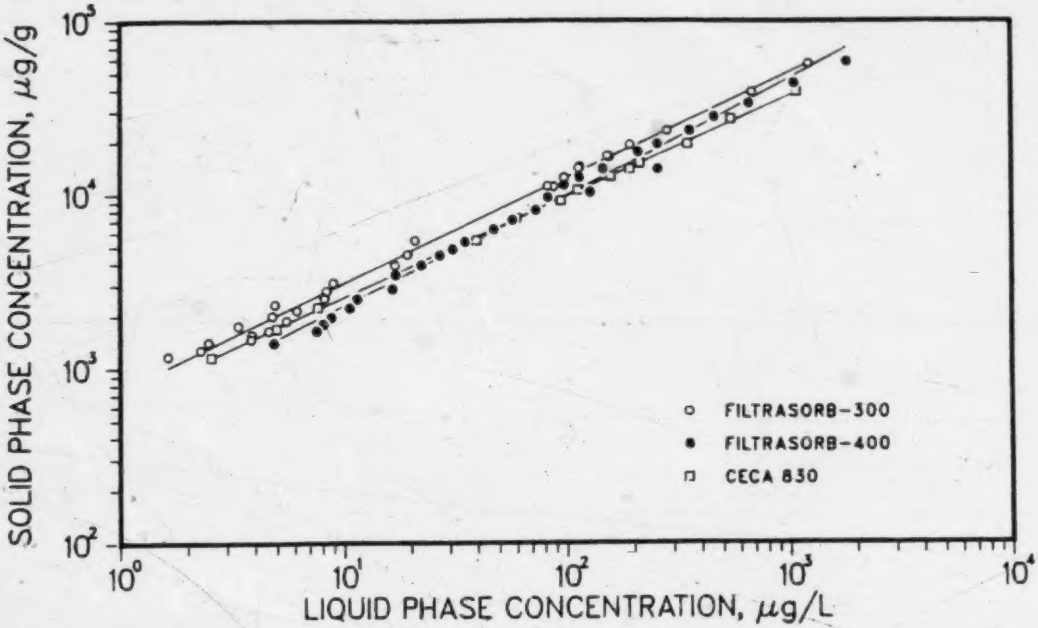

Figure III.3 Comparison of Dibromochloromethane Isotherms on F-300, Ceca 830 and F-400 Carbon

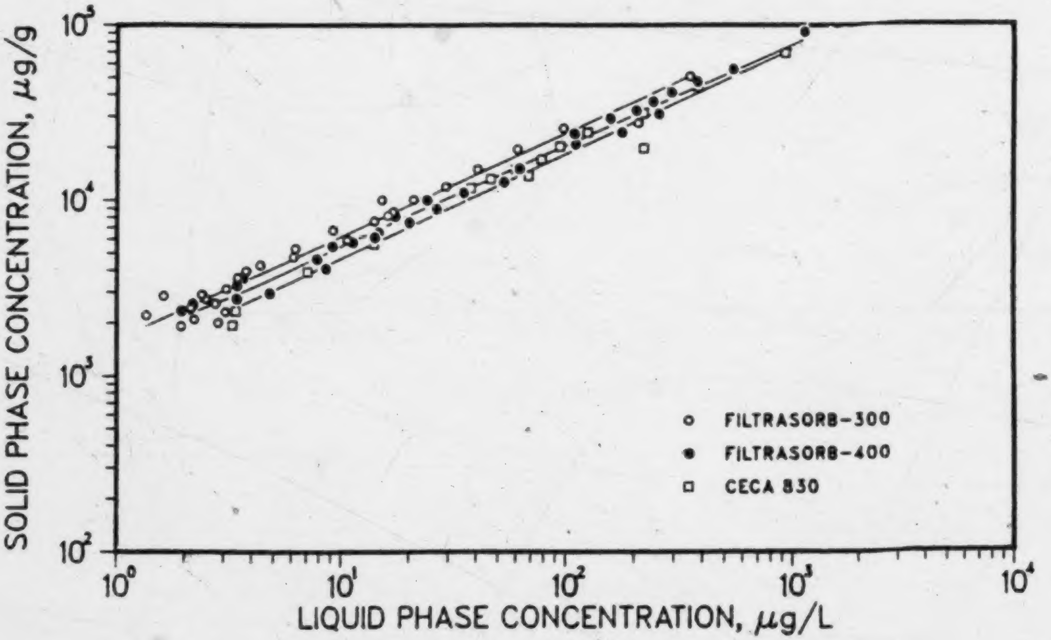

Figure III.4 Comparison of Bromoform Isotherms on F-300, Ceca 830 and F-400 Carbon

Appendix IV

Computer Programs Listings

```
C
C
C       **** MULTI-COMPONENT ISOTHERM PROGRAM ****
C
C
C           PREDICTS MULTICOMPONENT BOTTLE POINT ISOTHERM LIQUID AND SOLID
C      PHASE CONCENTRATIONS GIVEN THE SINGLE SOLUTE ISOTHERM PARAMETERS,
C      INITIAL CONCENTRATIONS, BOTTLE VOLUME, AND CARBON DOSAGES.  THREE
C      DIFFERENT ISOTHERM EXPRESSIONS CAN BE USED :
C
C       OPTION 1    FREUNDLICH (NEED K(MOLAR UNITS), 1/N, CO(MOLAR UNITS),
C                     FOR EACH COMPONENT.
C
C       OPTION 2    MYERS (NEED K(MOLAR UNITS), CO(MOLAR UNITS), P, H, FOR
C                     EACH COMPONENT)
C
C       OPTION 3    FREUNDLICH-SINGER (NEED K, 1/N, CO, AS IN OPTION 1,
C                     PLUS Q* (CUTOFF Q), FOR EACH COMPONENT)
C
C
C          IDEAL ADSORBED SOLUTION THEORY IS USED TO PREDICT MULTICOMPON
C      BEHAVIOR.  THE IAST EQUATIONS ARE SOLVED BY A NEWTON-RAPHSON
C      ALGORITHM, USING SUBROUTINE SIMUL TO SOLVE THE AUGMENTED JACOBIAN.
C
C                     REVISED BY R.ANDREWS APR. 8,1987.
C                    TO INCORPORATE CALCULATION OF APE's
C
C      THIS VERSION OF THE PROGRAM ALSO CALCULATES AVERAGE
C      PERCENTAGE ERRORS (APE's) BY COMPARING OBSERVED
C      EXPERIMENTAL DATA TO PREDICTED VALUES. NOTE:THIS CALCULATION
C      SHOULD ONLY BE PERFORMED WHEN USING A TWO COMPONENT CASE
C      WHERE COMPONENT 1 IS REPRESENTED BY HYPOTHETICAL FREUNDLICH
C      PARAMETERS (HC's). THE APE's ARE CALCULATED ONLY FOR
C      COMPONENT 2.
C
C
C      WHEN USING HC's AS INPUT DATA, THE OUTPUT K AND CO VALUES
C      FOR THE HC'S WILL BE GIVEN IN TERMS OF MOLAR CONCENTRATIONS
C
C
C       THE INPUT IS FREE FORMAT :
C
C       N,D,OP,OPT
C       M(1),V(1)
C       M(2),V(2)
C       .
C       :
C       M(D),V(D)
C       K(1),P(1),WM(1),CO(1),H(1)
C       .
C       :
C       K(N),P(N),WM(1),CO(N),H(N)
C
C       WHERE: V(I)= BOTTLE VOLUME (L)      REAL
C              N   = # OF COMPONENTS        INT
C              D   = # OF CARBON DOSAGES    INT
C              DX  = # OF LAB DOSAGES  INT
C              OP  = OPTION                 INT
```

```
C               OPT = OPTION                      INT
C                   = 1 WHEN USING HC's; ALLOWS
C                       APE's TO BE CALCULATED
C                   = 0 WHEN NOT USING HC's
C               M(I)= CARBON DOSAGE (MG)      REAL
C               K(I)= K FOR GIVEN OPTION      REAL
C               P(I)= 1/N(I) FOR OPTION 1 OR 3
C                   = P(I) FOR OPTION 2       REAL
C               CO(I)= INITIAL CONCENTRATION FOR CONPONENT I  REAL
C               H(I)= DUMMY FOR OPTION 1
C                   = H(I) FOR OPTION 2
C                   = Q*(I) FOR OPTION 3      REAL
C
C
      DIMENSION XK(12),XN(12),CO(12),Q(24,50),A(26,26),XZX(12),
     +     X(24),C(12,50),XH(12),V(50),CO1(12),
     + W(12),Z(12),S(12),QO(12),ERR(12),COO(10),
     + CEOBS(50),QEOBS(50),DSOBS(50)
       INTEGER P,I,D,OP,T,OPT
       REAL M(50),WM(6),MASS(50)
C.....READ DATA...#OF COMPS,#OF DOSAGES,# OF EXPERIMENTAL DOSAGES,OPTION,HC
      READ(4,*) N,D,OP,OPT
C.....READ DOSAGES AND VOLUMES...
C     HIREI=10.0**(ALOG10(DOMAX/DOMIN)/FLOAT(D))
      DO 20 I=1,D
      READ(4,*) M(I),V(I)
      MASS(I)=M(I)
       M(I) = M(I)/1000
   20 CONTINUE
C .....READ COMPONENT SINGLE SOLUTE PARAMETERS....
C
      DO 10 I=1,N
      READ(4,*) XK(I),XN(I),WM(I),CO(I),XH(I)
      CO(I)=CO(I)/WM(I)
      CONV=(WM(I)*(1/(WM(I)**(XN(I)))))
      XK(I)=XK(I)*(1/CONV)
        CO1(I) = CO(I)
       IF(OP .NE. 2) XN(I) = 1/XN(I)
C
C.....CALCULATE INITIAL GUESSES ON Q'S....
C
      Q(I,1) = 0.70*CO(I)*V(1)/M(1)
   10  CONTINUE
C
C     READ NUMBER OF EXPERIMENTAL DATA POINTS (FOR APE CALCULATION)
C
      READ(8,*) DX
C
C.....READ IN OBSERVED DATA, USED IN APE CALC.
C
       IF(OPT .EQ. 0) GO TO 18
       DO 8 I=1,DX
       READ(5,*) CEOBS(I),QEOBS(I),DSOBS(I)
    8  CONTINUE
  18  DO 11 I=1,N
  11  QO(I) = 1.0
        GO TO 113
C
```

```
      C.....FOR MYERS ISOTHERM USE NEWTON-RAPHSON TO FIND QO.(USED
      C         .TO CALCULATE DIMENSIONLESS Q....
      C
       113      CONTINUE
                XX = D
                JX = 1
                JXJ = 0
             IF (OP .EQ. 2) THEN
             DO 16 I=1,N
             QO(I) = CO(I)*V(1)/M(1)
             DQ = 0
             K = 0
        17   DQ=(LOG(CO(I)*XH(I))-LOG(QO(I))-XK(I)*QO(I)**XN(I))/
           +    (1/QO(I)+XK(I)*XN(I)*QO(I)**(XN(I)-1))
              IF(DQ .LE. -QO(I)) DQ = -0.9*QO(I)
              K = K + 1
      C
      C.....CONVERT K'S AND Q'S TO DIMENSIONLESS FOR MYERS ISOTHERM
      C
              IF(K .GT. 20) GO TO 19
             QO(I) = QO(I) +DQ
             IF(ABS(DQ) .GT. 1.E-4) GO TO 17
       15    XK(I) = XK(I)*QO(I)**XN(I)
      C       PRINT*, 'QO',I,'=',QO(I)
          16 Q(I,1) = Q(I,1)/QO(I)
              GO TO 25
      C
      C.....IF NEWTON RAPHSON FAILS TO CONVERGE, SET QO EQUAL TO 100.0....
      C
        19    WRITE(7,*) 'NEWTON-RAPHSON FAILED TO CONVERGE FOR DIMENSIONLESS
           + Q(I,J), STANDARD CORRECTIVE ACTION TAKEN'
              QO(I) = 100.0
              GO TO 15
       25     CONTINUE
      C
      C.....FOR FREUNDLICH-SINGER CALCULATE THE FIRST POINT USING FREUNDLICH
      C          THEN USE THIS AS AN INITIAL GUESS ON FREUNDLICH-SINGER....
      C
             ELSE IF(OP .EQ. 3) THEN
       43    U = 100
             JXJ = JXJ + 1
             D = JXJ
              JX = D
               IF(JX .GT. XX) GO TO 42
             OP = 1
             GO TO 13
        14   OP = 3
             U = 0
             END IF
      C
      C.....SOLVE EACH DOSAGE INDIVIDUALLY....
      C
        13   DO 40 J = JX,D
      C
      C.....SET THE ERROR CRITERIA FOR NEWTON-RAPHSON....
      C
             EPS = 1.E-3
      C
```

```
C.....SET COUNTER FOR ITERATIONS TO 0....
C
        YXZ = -22
        F = 0
        DD = 0
C
C.....ASSIGN INITIAL GUESSES ON Q'S....
C
      DO 30 I = 1,N
      IF (J .NE. 1) Q(I,J) = 0.50*Q(I,J-1)
   30  IF(CO(I) .LE. Q(I,J)*QO(I)*M(J)/V(J)) Q(I,J) = 0.999999*CO(I)*
     +     V(J)/(M(J)*QO(I))
      IF(OP .EQ. 2) THEN
C
C     ....CALCULATE DIMENSIONLESS H(I) FOR EACH DOSAGE (FOR MYERS) ...
C
      DO 39 I=1,N
   39 XH(I) = XH(I)*M(J)/V(J)
C
C.....ASSIGN VALUES FOR QO FOR MYERS *****
C
      DO 35 I = 1+N,2*N
      Q(I,J) = 2*Q(I-N,1)
 35   IF(J .NE. 1) Q(I,J) = 0.95*Q(I,J-1)
      ELSE
      END IF
C
C.....CALCULATE Q TOTAL AND THE SUM OF (N * Q)
C
   65 QT = 0
      XNQ = 0
      DO 70 L = 1, N
      QT = QT + Q(L,J)*QO(L)/QO(1)
   70 XNQ = XNQ + XN(L)*Q(L,J)
C
C.....CALCULATE JACOBIAN FOR FREUNDLICH ISOTHERM .......
C
       IF(OP .EQ. 1) THEN
      DO 50 I = 1. N
       E = Q(I,J)*((XNQ/(XN(I)*XK(I)))**XN(I))/QT
      DO 60 K = 1. N
       A(I,K) = +E/QT - XN(I)*XN(K)*E/XNQ
       IF(K .EQ. I) A(I,K)=-M(J)/V(J)-E/Q(I,J)+E/QT
     +    -E*XN(I)**2/XNQ
   60 CONTINUE
      A(I,N+1) = -CO(I) + M(J)*Q(I,J)/V(J) + E
   50 CONTINUE
       T = N
C
C.....CALCULATE JACOBIAN FOR FREUNDLICH SINGER .....
C
      ELSE IF(OP .EQ. 3) THEN
      B =0
      DO 91 I = 1,N
      W(I) = (-M(J)*Q(I,J)/V(J)+CO(I))*QT/Q(I,J)
      Z(I) = -XH(1)*(XN(1)-1)/2+XH(I)*(XN(I)-1)/2
   91 S(I) = XK(I)*W(I)**(1/XN(I))
      DO 92 I = 2,N
 92   B = B + XN(I)*Q(I,J)*S(1)/(XN(1)*S(1)+Z(I))**2
      DO 93 I =  1,N-1
      DO 94 K = 1,N+1
      A(I,K) = -S(I+1)/QT +S(1)/QT
      IF(K .EQ. 1) A(I,K) = -S(I+1)/QT+S(1)*(-M(J)*QT/(W(I)*Q(I,J)*V(J))
     +   +1/QT-1/Q(I,J))
      IF(K .EQ. I+1) A(I,K) = -S(K)*(-M(J)*QT/(V(J)*W(K)*Q(K,J))+1/QT-
     +   1/Q(1,J))+S(1)/QT
 94   IF(K .EQ. N+1) A(I,K) = +XN(I+1)*S(1+I)-XN(1)*S(1)-Z(I+1)
 93   CONTINUE
      DO 96 K = 1,N
      A(N,K) = -Q(1,J)/(S(1)*QT*XN(1))+XN(K)/(XN(1)*S(1)+Z(K))
     +   -B/QT
      IF(K .EQ.1) A(N,K) = 1/S(1)-(Q(1,J)/(S(1)*W(1)*XN(1))+B/W(1))
     +   *(-M(J)*QT/(V(J)*Q(1,J))+W(1)*(1/QT-1/Q(1,J)))
 96   CONTINUE
      A(N,N+1) = +1-Q(1,J)/S(1)
      DO 97 I = 2,N
 97   A(N,N+1) = A(N,N+1) - XN(I)*Q(I,J)/(XN(1)*S(1)+Z(I))
        T = N
      ELSE
C
C.....OR CALCULATE JACOBIAN FOR MYERS ISOTHERM .******
C
      DO 51 I = 1,N-1
      DO 61 K = 1,2*N+1
      A(I,K) = O
      IF(K .EQ. N+1) A(I,K)=(1+XK(1)*XN(1)*Q(N+1,J)**XN(1))*
     +     QO(1)/QO(I+1)
      IF(K .EQ. N+I+1) A(I,K)=-1-XK(I+1)*XN(I+1)*Q(N+I+1,J)**XN(I+1)
      IF(K .EQ. 2*N+1) A(I,K)=(-Q(N+1,J)-XK(1)*XN(1)/(1+XN(1))*Q(N+1
     + ,J)**(1+XN(1)))*QO(1)/QO(I+1)+Q(N+I+1,J)+XK(I+1)*XN(I+1)/
     +  (1+XN(I+1))*Q(N+I+1,J)**(1+XN(I+1))
 61   CONTINUE
 51   CONTINUE
      DO 55 I = 1,N
      DO 58 K = 1,2*N+1
      A(I+N-1,K) = O
      IF(K .LE. N) A(I-1+N,K) = QO(K)/(QO(1)*QT)
      IF(K .EQ. I) A(I+N-1,K) =-1/(CO(I)*V(J)/(M(J)*QO(I))-Q(I,J))
     +    -1/Q(I,J)+QO(I)/(QO(1)*QT)
      IF(K .EQ. I+N) A(I+N-1,K)=-1/Q(N+I,J)-XN(I)*XK(I)*Q(N+I,J)**
     +   (XN(I)-1)
      IF(K .EQ. 2*N+1) A(N+I-1,K)=-LOG(CO(I)*V(J)/(M(J)*QO(I))-Q(I,J))
     ++LOG(Q(I,J)*Q(I+N,J)*QO(I)/(QT*XH(I)*QO(1)))+XK(I)*Q(I+N,J)**XN(I)
 58     CONTINUE
 55   CONTINUE
      DO 64 K = 1,2*N
      IF(K .GT. N) A(2*N,K) = -Q(K-N,J)/Q(K,J)**2
 64   IF(K .LE. N) A(2*N,K) = 1/Q(K+N,J)
      A(2*N,2*N+1) = +1
      DO 66 I = 1,N
 66   A(2*N,2*N+1) = A(2*N,2*N+1) -Q(I,J)/Q(N+I,J)
       T = N*2
      ENDIF
C
C.....CALL SUBROUTINE SIMUL TO SOLVE JACOBIAN ******
C
```

```
          CALL SIMUL(T,A,X,1.E-12,0,26,DETER)
C
C.....COUNT ITERATIONS *******
C
            F = F + 1
           IF(F.EQ.1.0.AND.YXZ.EQ.-22.0) THEN
             DO 555 I=1,N
  555        XZX(I) = X(I)
             ENDIF
C
C.....IF MORE THEN 20 ITERATIONS USE MODIFIED BROYDENS METHOD ON INTERVAL
C        FROM -2*DQ TO 2*DQ
C
            IF(F .GT. 20.0)  THEN
          YXZ = YXZ + 2.0
          F = 0.0
          IF(YXZ .EQ. 40.0) GO TO 191
          DO 52 I=1,N
          Q(I,J) = Q(I,J)+YXZ*XZX(I)/20.0
   52      IF(Q(I,J) .LE. 0.0) Q(I,J) = 0.00001
          GO TO 82
          ENDIF
         IF(OP .EQ. 2) N = N*2
C
C.....CHECK FOR  CONVERGENCE ******
C
         DO 80 I = 1, N
         IF(ABS(X(I)) .LT. EPS) GO TO 80
C
C.....ELIMINATE NEGATIVE ROOTS ******
C
         DO 90 K = 1,N
          IF(X(K) .LT. -Q(K,J))  X(K) = -0.95*Q(K,J)
    90 Q(K,J) = Q(K,J) + X(K)
         IF(OP .EQ. 2) N = N/2
C
C.....CHECK THAT MASS ISN'T CREATED ******
C
   82   DO 83 G = 1,N
   83   IF((CO(G)-M(J)*QO(G)*Q(G,J)/V(J)) .LE. 0.0) Q(G,J)=0.999999/QO(G)
     +    *CO(G)*V(J)/M(J)
C
C.....IF DIDN'T CONVERGE, REITERATE ******
C
        GO TO 65
    80 CONTINUE
        IF(OP .EQ. 2) N = N/2
C
C.....IF CONVERGENCE, CALCULATE THE LIQUID CONCENTRATIONS ****
C
        DO 100 I = 1, N
  100   C(I,J)=CO(I)-(M(J)/V(J))*QO(I)*Q(I,J)
C
C.....PUT CALCULATED VALUES FOR Q BACK INTO IAS EQUATIONS AND
C           COMPARE LIQUID CONCENTRATIONS TO MASS BALANCE VALUES....
C
C.....FOR FREUNDLICH .......
C
```

```
      IF(OP .EQ. 1) THEN
      DO 31 I=1,N
      XL = Q(I,J)/QT*(XNQ/(XN(I)*XK(I)))**XN(I)
   31 ERR(I) = ABS((XL-C(I,J))/C(I,J))
C
C..... FOR FRUENDLICH SINGER .......
C
      ELSEIF(OP .EQ. 3) THEN
        DO 32 I=1,N-1
   32 ERR(I) = ABS(XN(I+1)*S(I+1)-XN(1)*S(1)-Z(I+1))/10
      ERR(N) = 1-Q(1,J)/S(1)
      DO 33 I=2,N
   33 ERR(N) = ERR(N) - XN(I)*Q(I,J)/(XN(1)*S(1)+Z(I))
      ERR(N) = ABS(ERR(N))/10
      ELSE
C
C..... OR FOR MYERS. *******
C
      DO 37 I=1,N
      XL=Q(I,J)*Q(N+I,J)*QO(I)**2*M(J)/(XH(I)*V(J)*QT*QO(1))
     +    *EXP(XK(I)*Q(N+I,J)**XN(I))
   37 ERR(I) = ABS((XL-C(I,J))/C(I,J))
      ENDIF
C
C.....IF ERROR BETWEEN C CALCULATED FROM IAS EQUATIONS AND FROM
C              THE MASS BALANCE IS GREATER THEN 0.1% CHANGE ERROR CRITERIA
C              FOR NEWTON-RAPHSON AND REITERATE (MAXIMUM 10 TIMES)
C
      DO 36 I=1,N
      IF(ERR(I) .GT. 1.0)THEN
       DD = DD + 1
       IF(DD .EQ. 10.0) GO TO 40
      EPS = 0.1*EPS
      F = 0
      GO TO 65
      ENDIF
   36 CONTINUE
C
C.....GO TO NEXT DOSAGE *******
C
C      PRINT*, 'J=',J
   40 CONTINUE
      IF(U .EQ. 100) GO TO 14
C          PRINT*, 'J =',J
      IF(OP.EQ. 3) GO TO 43
C
C.....PRINT RESULTS   ********
C
 42   WRITE(7,1000) 'K IN (UG/G)(L/UG)**1/N  C IN (uG/L)  Q IN (uG/G)'
      DO 115 P = 1,N,4
      WRITE(7,1001) 'CARBON DOSAGE','COMPONENT',P,'COMPONENT',(P+1)
     +    ,'COMPONENT',(P+2),'COMPONENT',(P+3)
 1001 FORMAT(//,2X,A,T21,A,T32,I1,T43,A,T54,I1,T65,A,T76,I1,T87,A,
     +T98,I1)
      WRITE(7,1004)
 1004 FORMAT(/,T7,'(MG)',T22,'C',T31,'Q',T44,'C',T53,'Q',T66
     +    ,'C',T75,'Q',T88,'C',T97,'Q',/)
      DO 120 I = 1,D
      TQN=0.0
      DO 121 J=1,N
  121 TQN=Q(J,I)*XN(J)*QO(P)+TON
C     DO 122 IJ=P,P+3
      DO 122 IJ=P,P-1+N
  122 COO(IJ)=(TQN/XN(IJ)/XK(IJ))**XN(IJ)
  120 WRITE(7,1005) 1000*M(I),C(P,I)*WM(1),Q(P,I)*QO(P)*WM(1)
     +,C(P+1,I)*WM(2),Q(P+1,I)*QO(P+1)*WM(2),C(P+2,I)*WM(3)
     +,Q(P+2,I)*QO(P+2)*WM(3),C(P+3,I)*WM(4),Q(P+3,I)*QO(P+3)*WM(4)
C
      DO 180 I=1,D
  180 WRITE(6,1007) C(P,I)*WM(1),Q(P,I)*QO(P)*WM(1)
     +,C(P+1,I)*WM(2),Q(P+1,I)*QO(P+1)*WM(2),C(P+2,I)*WM(3)
     +,Q(P+2,I)*QO(P+2)*WM(3),C(P+3,I)*WM(4),Q(P+3,I)*QO(P+3)*WM(4)
C 120 WRITE(7,1005)1000*M(I),C(P,I)
  115 CONTINUE
      IF (OPT .EQ. 0) GO TO 200
C
C.....CALC APE VALUES
C
      APEQ=0
      APEC=0
      COUNT=0
      VALUEQ=0
      VALUEC=0
      DO 123 I=1,D
      COUNT=COUNT+1
      DO 125 J=1,D
  124 IF (MASS(I) .EQ. DSOBS(J)) GO TO 119
  125 CONTINUE
  119 ERRORQ=(ABS(QEOBS(J)-(Q(2,I)*QO(2)*WM(2))))/QEOBS(J)
      VALUEQ=VALUEQ+ERRORQ
      ERRORC=(ABS(CEOBS(J)-(C(2,I)*WM(2))))/CEOBS(J)
      VALUEC=VALUEC+ERRORC
  123 CONTINUE
      APEQ=(100/COUNT)*VALUEQ
      APEC=(100/COUNT)*VALUEC
  200 DO 130 I = 1,N
  130 WRITE(7,1006) 'COMPONENT',I,':',XK(I)*(WM(I)*(1/(WM(I)**(1/XN
     +(I))))),1/XN(I),CO(I)*WM(I)
 1000 FORMAT(/,A//)
 1005 FORMAT(' ',T1,F8.2,T16,E10.4,T27,E10.4,T38,E10.4,T49,E10.4,
     +            T60,E10.4,T71,E10.4,T82,E10.4,T93,E10.4)
C    + ,3E10.3)
 1006 FORMAT(/,A,T11,I1,T14,A,T17,'K =',F9.2,2X,'1/N =',F7.5,
     +      2X,'CO =',F9.4)
 1007 FORMAT(' ',8F12.4)
C
C.....PRINT APE VALUES
C
      IF (OPT .EQ. 0) GO TO 210
      WRITE(7,1500) 'COMPONENT 2',':',APEC,APEQ
 1500 FORMAT(//,A,T14,A,T17,'APE C (%) = ',F6.2,2X,'APE Q (%) = '
     +,F6.2)
C         'HALT'
  210 STOP
  191     PRINT*, 'NEWTON-RAPHSON  FAILED TO CONVERGE AFTER 20 CYCLES'
          STOP

          END
      C
      C
      C           ******HYPOTHETICAL COMPONENT PROGRAM*******
      C
      C       THIS PROGRAM WILL PREDICT ISOTHERMS BY USING ONE TO SIX
      C     HYPOTHETICAL COMPONENTS TO REPRESENT THE BACKGROUND COMPETITION.
      C     SINCE IT WILL USE IMSL ROUTINES, IT WILL NEED TO BE COMPILED IN IBM
      C     PROFESSIONAL FORTRAN.  IMSL LIBRARY ZERXTD MUST BE USED.  THIS
      C     LIBRARY CONTAINS BOTH ZSPOW AND ZXSSQ.
      C
      C       SINCE THERE ARE THREE FREUNDLICH PARAMETERS FOR EACH HYPOTHETICAL
      C     COMPONENT, THERE IS A MAXIMUM OF 18 PARAMETERS THAT CAN BE USED.
      C     THIS PROGRAM WILL LET YOU DECIDE WHICH OF THE FREUNDLICH PARAMETERS
      C     WILL BE VAIRIED BY THE PROGRAM.  IT IS SUGGESTED THAT YOU DO NOT
      C     VARY ALL 18 PARAMETERS BECAUSE THE PROGRAM WILL RUN VERY SLOWLY.
      C
      C       THE RESIDUALS CAN BE CALCULATED TWO WAYS.  ONE WAY IS TO USE
      C     THE CHANGE IN THE LIQUID CONCENTRATIONS ARE THE RESIDUAL (RES=0).
      C     TAND HE OTHER WAY IS TO USE THE NORMALIZED CHANGE IN THE LIQIUD
      C     CONCENTRATIONS AS THE RESIDUAL (RES=1).
      C
      C     PROGRAM WRITTEN BY:  THOMAS FRANCIS SPETH
      C
      C     SPECIAL THANKS TO: PAUL LUFT, AND DR. JOHN CRITTENDEN FOR THEIR
      C     PREVIOUS WORK.
      C
      C               ***VARIABLE DEFINITIONS***
      C
      C      AA    = 0(NO), 1(YES) - IS PREVIOUS PARAMETER IS TO BE VARIED?
      C      CE    = RAW EQUILIBRIUM CONCENTRATIONS FOR KNOWN COMPONENT (ug/L)
      C      CHAR  = NAME OF THE KNOWN COMPOUND
      C      CI    = EQUILIBRIUM LIQUID CONCENTRATIONS FROM IAST
      C      CO    = INITIAL CONCENTRATION OF KNOWN COMPONENT (ug/L)
      C      D     = NUMBER OF BOTTLE POINTS
      C      DM    = DOSAGES OF CARBON (mg)
      C      DELTA = THIRD CONVERGENCE CRITERIA (SET TO ZERO)
      C      EPS   = SECOND CONVERGENCE CRITERIA (SUM OF THE SQUARES OF THE
      C              RESIDUALS:  CAN BE SET TO ZERO)
      C      F     = OUTPUT CONTAINING RESIDUALS
      C      HC    = NAME OF HYPOTHETICAL COMPONENT
      C      IC    = COUNTER
      C      IAST  = SUBROUTINE THAT CALCULATES RESIDUALS OF CE (IAST PROGRAM)
      C      IER   = ERROR PARAMETER
      C      INFER = INDICATES WHICH CONVERGENCE CRITERIA WAS SATISFIED
      C      IOPT  = INPUT OPTIONS PARAMETER (0,1,or 2:  SEE MANUAL)
      C      IXJAC = INPUT ROW DIMENSION OF MATRIX XJAC
      C      J     = COUNTER
      C      K     = FREUNDLICH ISOTHERM PARAMETER (um/g)*(L/um)**1/n  TRACER
      C      M     = NUMBER OF ORIGINALS OR OBSERVATIONS
      C      MAXFN = MAXIMUM NUMBER OF FUNCTION EVALUATIONS
      C      MW    = MOLECULAR WEIGHT OF KNOWN COMPONENT
      C      MWHC  = MOLECULAR WEIGHTS OF THE HYPOTHETICAL COMPONENTS
      C      NA    = NUMBER OF UNKNOWN PARAMETERS
      C      NN    = NUMBER OF HYPOTHETICAL COMPONENTS
      C      NSIG  = FIRST CONVERGENCE CRITERIA (NUMBER OF SIGNIFICANT DIGITS)
      C      P     = INITIAL PARAMETER GUESSES FOR H.C.'S
      C      PARM  = INPUT VECTOR (ONLY USED WHEN IOPT=2)
      C      PD    = PERCENT DIFFERENCE BETWEEN CE(EXP) AND CI(IAST)
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C      QI     = SOLID CONCENTRATION (ug/g)
C      RES    = COUNTER TO DETERMINE WHICH RESIDUAL IS TO BE USED
C      SSQ    = RESIDUALS SUM OF SQUARES
C      V      = VOLUMES OF BOTTLES (L)
C      WORK   = WORK VECTOR (USED ONLY WHEN IOPT=2)
C      X      = PARAMETER VALUES
C      XJAC   = OUTPUT CONTAINING JACOBIAN
C      XJTJ   = OUTPUT (XJAC-TRANSPOSED)
C      XN     = FRUENDLICH ISOTHERM PARAMETER 1/n  TRACER
C      ZXSSQ  = SUBROUTINE USED TO FIT THE DATA
C
C
C                    ***INPUT***
C
C      CHAR,D,K,XN,CO,MW
C      DM(1),V(1),CE(1)
C      DM(2),V(2),CE(2)
C      ..     ..    ..
C      DM(D),V(D);CE(D)
C      NN
C      HC1,K(HYP1),AA(1), 1/N(HYP1),AA(2), CO(HYP1),AA(3), MWHC(HYP1)
C      (THE FOLLOWING ARE USED IF NEEDED.)
C      HC2,K(HYP2),AA(4), 1/N(HYP2),AA(5), CO(HYP2),AA(6), MWHC(HYP2)
C      HC3,K(HYP3),AA(7), 1/N(HYP3),AA(8), CO(HYP3),AA(9), MWHC(HYP3)
C      HC4,K(HYP4),AA(10),1/N(HYP4),AA(11),CO(HYP4),AA(12),MWHC(HYP4)
C      HC5,K(HYP5),AA(13),1/N(HYP5),AA(14),CO(HYP5),AA(15),MWHC(HYP5)
C      HC6,K(HYP6),AA(16),1/N(HYP5),AA(17),CO(HYP6),AA(18),MWHC(HYP6)
C      RES
C      NSIG, EPS, DELTA, IOPT
C
C      WHERE, (HYP) REFERS TO THE ORIGINAL GUESSES OF THE FRUENDLICH
C      CONSTANTS FOR THE HYPOTHETICAL COMPONENTS. THE UNITS OF THE
C      HYPOTHETICAL COMPONENTS ARE:  (um/ug)(L/um)**1/n FOR K(HYP),
C      AND (ug/L) FOR CO(HYP).  IF YOU WISH TO INPUT CO(HYP) IN
C      UNITS OF (um/L), ENTER 1.0 FOR ITS MOLECULAR WEIGHT.
C
C         HYPOTHETICAL COMPONENTS TWO THROUGH SIX MAY OR MAY NOT
C      BE NEEDED.
C
C         THE VARIABLES AA(1) THROUGH AA(16) ARE INTEGERS USED TO
C      DETERMINE WHICH PARAMETERS ARE TO BE VARIED.  IF IT IS 1 THE
C      PREVIOUS PARAMETER IS TO BE VARIED.  IF IT IS 0 THE PREVIOUS
C      PARAMETER IS NOT TO BE VARIED.  FOR EXAMPLE, IF AA(3) IS 1, THE
C      PARAMETER CO(HYP1) IS TO BE VARIED IN THE PROGRAM.
C
C         IF A REASONABLY SMALL NSIG IS BEING USED, EPS CAN BE SET TO
C      ZERO.  THE PROGRAM WILL FINISH WHEN EITHER OF THE CONVERGENCE
C      CRITERIA IS SATISFIED.  IOPT SHOULD BE SET TO ZERO.  IF THE
C      RUN FAILS, WHICH IT SHOULDN'T, THEN CONSIDERATION SHOULD BE
C      MADE TO WHETHER IOPT SHOULD BE CHANGED.  CHANGING IOPT TO
C      1 IS RECOMMENDED IF IOPT IS TO BE CHANGED.  IF 2 IS CHOSEN,
C      PARM(1 -4) ARE TO BE INSERTED, IN ORDER, ON THE FOLLOWING
C      LINE.
C
C      DELTA SHOULD/CAN BE SET TO ZERO.
C
C                ********PROGRAM********
C
```

```
C                  ***DIMENSIONS***
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      EXTERNAL IAST
      DOUBLE PRECISION MW,K,MWHC
      DIMENSION PARM(4),X(18),F(50),XJAC(50,18),XJTJ(171),WORK(361),
     $CE(50),PD(50),CI(7,50),V(50),QI(7,50),MWHC(6),P(18),B(18),DM(50)
      CHARACTER*12 CHAR,HC(6)
      CHARACTER*1 SR(18)
      INTEGER D,RES,AA(18)
      COMMON /ZSQ/ DM,CO,V,K,XN,D,CE,NN,RES,MW,P,AA,B,CI,QI,NC
C
C                 ***OPEN FILES***
C
C       OPEN(UNIT=4,FILE='HC.DAT')
C       OPEN(UNIT=7,FILE='HC.OUT')
C
C                ***READ DATA***
C
C       PRINT*, 'READING DATA'
      READ(4,*) CHAR,D,K,XN,CO,MW
      XN=1.0D0/XN
      CO=CO/MW
      DO 10 I=1,D
       READ(4,*) DM(I),V(I),CE(I)
       DM(I)=DM(I)/1000.0D0
       CE(I)=CE(I)/MW
 10   CONTINUE
C
C           ***READ INITIAL PARAMETER GUESSES***
C
      READ(4,*) NN
      READ(4,*) HC(1),P(1),AA(1),P(2),AA(2),P(3),AA(3),MWHC(1)
      IF (NN .GE. 2) READ(4,*) HC(2),P(4),AA(4),P(5),AA(5),P(6),
     $AA(6),MWHC(2)
      IF (NN .GE. 3) READ(4,*) HC(3),P(7),AA(7),P(8),AA(8),P(9),
     $AA(9),MWHC(3)
      IF (NN .GE. 4) READ(4,*) HC(4),P(10),AA(10),P(11),AA(11),
     $P(12),AA(12),MWHC(4)
      IF (NN .GE. 5) READ(4,*) HC(5),P(13),AA(13),P(14),AA(14),
     $P(15),AA(15),MWHC(5)
      IF (NN .EQ. 6) READ(4,*) HC(6),P(16),AA(16),P(17),AA(17),
     $P(18),AA(18),MWHC(6)
      READ(4,*) RES
      READ(4,*) NSIG,EPS,DELTA,IOPT
      IF (IOPT .EQ. 2) THEN
       READ(4,*) PARM(1),PARM(2),PARM(3),PARM(4)
      ENDIF
C
C             ***WRITE INITIAL PARAMETER GUESSES***
C
      WRITE(7,15)
 15   FORMAT(10X,'INITIAL H.C. GUESSES',//)
      WRITE(7,18)
 18   FORMAT(1X,'COMPONENT',T15,'K (um/g)(L/um)**1/n',T38,'1/n',T48,
     $'CO (ug/L)',T63,'M.W.',/)
      DO 20 I=1,NN*3
       IF (AA(I) .EQ. 1) SR(I)='*'
```

```
        IF (AA(I) .NE. 1) SR(I)=' '
 20    CONTINUE
       WRITE(7,50) HC(1),P(1),SR(1),P(2),SR(2),P(3),SR(3),MWHC(1)
        IF (NN .GE. 2) WRITE(7,50) HC(2),P(4),SR(4),P(5),SR(5),
     $P(6),SR(6),MWHC(2)
        IF (NN .GE. 3) WRITE(7,50) HC(3),P(7),SR(7),P(8),SR(8),
     $P(9),SR(9),MWHC(3)
        IF (NN .GE. 4) WRITE(7,50) HC(4),P(10),SR(10),P(11),SR(11),
     $P(12),SR(12),MWHC(4)
        IF (NN .GE. 5) WRITE(7,50) HC(5),P(13),SR(13),P(14),SR(14),
     $P(15),SR(15),MWHC(5)
        IF (NN .EQ. 6) WRITE(7,50) HC(6),P(16),SR(16),P(17),SR(17),
     $P(18),SR(18),MWHC(6)
 50     FORMAT(1X,A10,T16,F9.4,1X,A1,T33,F9.4,1X,A1,T46,F9.3,1X,
     $A1,T60,F8.3)
C
C                ***CONVERT INITIAL PARAMETERS***
C
       P(2)=1.0D0/P(2)
       P(3)=P(3)/MWHC(1)
       IF (NN .GE. 2) THEN
        P(5)=1.0D0/P(5)
        P(6)=P(6)/MWHC(2)
       ENDIF
       IF (NN .GE. 3) THEN
        P(8)=1.0D0/P(8)
        P(9)=P(9)/MWHC(3)
       ENDIF
       IF (NN .GE. 4) THEN
        P(11)=1.0D0/P(11)
        P(12)=P(12)/MWHC(4)
       ENDIF
       IF (NN .GE. 5) THEN
        P(14)=1.0D0/P(14)
        P(15)=P(15)/MWHC(5)
       ENDIF
       IF (NN .EQ. 6) THEN
        P(17)=1.0D0/P(17)
        P(18)=P(18)/MWHC(6)
       ENDIF
C
C                    ***COUNT PARAMETERS TO BE VARIED***
C
       NA=0
       DO 60 I=1,NN*3
        IF (AA(I) .EQ. 1) NA=NA+1
 60    CONTINUE
C
C               ***ASSIGN PARAMETERS FOR ZXSSQ***
C
       M=0
       IXJAC=50
       MAXFN=300
       IC=1
       DO 80 I=1,NN*3
        IF (AA(I) .EQ. 1) THEN
         X(IC)=P(I)
         IC=IC+1
        ENDIF
 80   CONTINUE
C
C  ***CALL ZXSSQ TO FIT THE SINGLE SOLUTE DATA TO MULTICOMPONENT DATA***
C
C       PRINT*, 'CALLING ZXSSQ'
      CALL ZXSSQ(IAST,M,NA,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,SSQ,F,XJAC,
     $IXJAC,XJTJ,WORK,INFER,IER)
C       PRINT*, 'LEAVING ZXSSQ'
C
C
C             ***WRITE ERROR***
C
      IF (IER .EQ. 133) THEN
       WRITE(7,125)
 125   FORMAT(1X,'THE MAXIMUM NUMBER OF ITERATIONS HAS BEEN EXCEEDED')
      ENDIF
C
C             ***CALCULATE THE PERCENT DIFFERENCE***
C
      DO 150 J=1,D
       PD(J)=(CE(J)-CI(1,J))/CE(J)*100.0D0
 150  CONTINUE
C
C                   ***PUT UNITS BACK TO ug ***
C
      DO 200 J=1,D
       CE(J)=CE(J)*MW
       DO 190 I=1,NC
        IF (I .EQ. 1) THEN
         CI(I,J)=CI(I,J)*MW
         QI(I,J)=QI(I,J)*MW
        ELSE
         CI(I,J)=CI(I,J)*MWHC(I-1)
         QI(I,J)=QI(I,J)*MWHC(I-1)
        ENDIF
 190   CONTINUE
       DM(J)=DM(J)*1000.0D0
 200  CONTINUE

C
C                ***PRINT OUT***
C
C      PRINT*, 'PRINTING OUTPUT'
      WRITE(7,300) CHAR
 300  FORMAT(//,1X,'HYPOTHETICAL COMPONENTS USING   ',A10,'AS THE TRACER
     $')
      IF (RES .EQ. 0) WRITE(7,310)
      IF (RES .EQ. 1) WRITE(7,311)
 310  FORMAT(1X,'(RESIDUALS= C(EXP)-C(PRED))')
 311  FORMAT(1X,'(RESIDUALS= (C(EXP)-C(PRED))/C(EXP))')
      WRITE(7,400)
 400  FORMAT(//,1X,'COMPONENT',T18,'K (um/g)(L/um)**1/n',T40,'1/N',
     $T52,'CO  (um/L)',/)
      WRITE(7,420) CHAR,K,1/XN,CO
      WRITE(7,420) HC(1),B(1),1.0D0/B(2),B(3)
      IF (NN .GE. 2) WRITE(7,420) HC(2),B(4),1.0D0/B(5),B(6)
      IF (NN .GE. 3) WRITE(7,420) HC(3),B(7),1.0D0/B(8),B(9)
      IF (NN .GE. 4) WRITE(7,420) HC(4),B(10),1.0D0/B(11),B(12)
      IF (NN .GE. 5) WRITE(7,420) HC(5),B(13),1.0D0/B(14),B(15)
      IF (NN .EQ. 6) WRITE(7,420) HC(6),B(16),1.0D0/B(17),B(18)
  420 FORMAT(2X,A10,T19,F10.4,T36,F9.4,T50,F9.3)
      WRITE(7,425)
  425 FORMAT(//,1X,'TRACER RESULTS')
      WRITE(7,430)
  430 FORMAT(//,1X,'DOSAGE (mg)',T17,'C (EXP)',T29,'C (IAST)',T41,
     $'Q (IAST)',T53,'% DIFFERENCE',/,1X,T18,'(ug/L)',T30,'(ug/L)'
     $,T42,'(ug/g)',T57,'IN C',/)
      DO 450 J=1,D
       WRITE(7,440) DM(J),CE(J),CI(1,J),QI(1,J),PD(J)
  440 FORMAT(1X,F9.4,T15,F9.3,T27,F9.3,T39,F10.3,T54,F8.2)
C      WRITE(6,445) CI(1,J),QI(1,J)
C445   FORMAT(F9.3,F10.3)
  450 CONTINUE
      WRITE(7,451) HC(1),HC(2),HC(3)
  451 FORMAT(///,1X,T19,A12,T36,A12,T56,A12,/,2X,'DOSAGE')
      WRITE(7,452)
  452 FORMAT(3X,'(mg)',T12,'C (ug/L)',T22,'Q (ug/g)',T33,'C (ug/L)'
     $,T43,'Q (ug/g)',T54,'C (ug/L)',T64,'Q (ug/g)',/)
      DO 455 J=1,D
       WRITE(7,453) DM(J),CI(2,J),QI(2,J),CI(3,J),QI(3,J),CI(4,J)
     $,QI(4,J)
  453 FORMAT(1X,F8.3,T10,F9.5,T20,F10.3,T31,F9.5,T41,F10.3,T52,F9.5,
     $T62,F10.3)
       WRITE(6,454) CI(1,J),QI(1,J),CI(3,J),QI(3,J),CI(4,J),QI(4,J)
     $,CI(5,J),QI(5,J)
  454 FORMAT(8F10.3)
  455 CONTINUE
      IF (NC .GT. 4) THEN
       WRITE(7,451) HC(4),HC(5),HC(6)
       WRITE(7,452)
       DO 458 J=1,D
        WRITE(7,453) DM(J),CI(5,J),QI(5,J),CI(6,J),QI(6,J),CI(7,J)
     $,QI(7,J)
  458  CONTINUE
      ENDIF
      WRITE(7,459) EPS,NSIG
  459 FORMAT(//,1X,'EPS= ',F10.6,5X,'NSIG= ',I2)
      WRITE(7,460) WORK(5)
  460 FORMAT(1X,'THE NUMBER OF ITERATIONS =',F6.1)
      WRITE(7,470) WORK(3)
  470 FORMAT(1X,'THE ESTIMATED NUMBER OF SIGNIFICANT FIGURES IN THE',/,
     $1X,'PARAMETERS =',F6.1)
      WRITE(7,480) SSQ
  480 FORMAT(1X,'THE RESIDUAL SUMS OF SQUARES =',F20.10)
C
      IF (INFER .EQ. 1) WRITE(7,510)
      IF (INFER .EQ. 2) WRITE(7,520)
      IF (INFER .EQ. 3) THEN
       WRITE(7,510)
       WRITE(7,520)
      ENDIF
      IF (INFER .EQ. 4) WRITE(7,540)
      IF (INFER .EQ. 5) THEN
       WRITE(7,510)
       WRITE(7,540)
      ENDIF
      IF (INFER .EQ. 6) THEN
       WRITE(7,520)
       WRITE(7,540)
      ENDIF
      IF (INFER .EQ. 7) THEN
       WRITE(7,510)
       WRITE(7,520)
       WRITE(7,540)
      ENDIF
510   FORMAT(1X,'NO. OF SIGNIFICANT FIGURES CRITERION WAS SATISFIED')
520   FORMAT(1X,'CHANGE IN SUM OF SQUARES CRITERION WAS SATISFIED')
540   FORMAT(1X,'GRADIENT CRITERION WAS SATISFIED')
      WRITE(7,560)
560   FORMAT(/,1X,'* = PARAMETER IS VARIED IN PROGRAM')
1000  STOP
      END
C
C
C     ********************SUBROUTINE IAST**********************
C
C
C       GIVEN THE FRUENDLICH PARAMETERS FOR THE HYPOTHETICAL
C     COMPONENTS WHICH ARE GENERATED IN ZXSSQ, THIS SUBROUTINE
C     WILL CALCULATE THE LIQUID CONCENTRATION RESIDUALS.  THIS
C     PROGRAM IS BASICALLY THE IAST PROGRAM.
C
C                   ***VARIABLE DEFINITIONS***
C
C      AA    = 0(NO), 1(YES) -IS PREVIOUS PARAMETER TO BE VARIED?
C      B     = FREUNDLICH PARAMETERS TO BE SENT BACK TO PROGRAM
C      CI    = CALCULATED LIQUID-PHASE CONC. (ug/L)- USING IAST
C      CE    = LIQUID-PHASE CONCENTRATIONS (ug/L) - FROM HC PROGRAM
C      CO    = INITIAL CONCENTRATIONS (um/L) -FROM HC PROGRAM
C      D     = NUMBER OF BOTTLE POINTS -FROM HC PROGRAM
C      DM    = DOSAGES OF CARBON (ug)-FROM HC PROGRAM
C      F     = OUTPUT CONTAINING THE RESIDUALS
C      FCN   = SUBROUTINE THAT SETS UP THE NON-LINEAR EQUATIONS
C      FNORM = OUTPUT: EQUAL TO F(1)**2+...F(NC)**2 AT POINT X
C      I     = COUNTER
C      IER   = ERROR PARAMETER
C      ITMAX = THE MAXIMUM NUMBER OF ITERATIONS
C      J     = COUNTER FOR EACH DOSAGE
C      KO    = COUNTER
C      K     = FRUENDLICH K (um/g)(L/um)**1/n -FROM HC PROGRAM
C      L     = COUNTER FOR ADJUSTING ZZ WHEN ERROR IS PRESENT
C      LP    = COUNTER FOR ITERATIONS
C      M     = NUMBER OF DOSAGES
C      MW    = MOLECULAR WEIGHT OF KNOWN COMPONENT -FROM HC PROGRAM
C      N     = NUMBER OF UNKNOWN PARAMETERS
C      NC    = NUMBER OF COMPONENTS
C      NSIGG = NUMBER OF DIGITS OF ACCURACY DESIRED IN COMPUTED ROOT
C      P     = INITIAL PARAMETER GUESS
C      PAR   = PARAMETER SET
C      PAR(1 TO NC)= FRUENDLICH K VALUES
C      PAR(10 TO 10+NC)=FREUNDLICH N VALUES
C      PAR(20 TO 20+NC)= INITIAL CONCENTRATIONS
C      PAR(30)= CARBON DOSAGE
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C      PAR(40)= VOLUME OF ISOTHERM BOTTLE
C      QI     = SOLID PHASE CONCENTRATION (ug/g)
C      QT     = TOTAL SURFACE LOADINGS (ug/g)
C      QNQ    = SUM OF Q*XN
C      RES    = COUNTER TO DETERMINE WHICH RESIDUAL IS TO BE USED
C      V      = VOLUMES OF BOTTLES (L) -FROM HC PROGRAM
C      WK     = WORK VECTOR:  LENGTH=N*(3*N+15+)/2
C      X      = FRUENDLICH PARAMETER VALUES
C      XX     = SOLID-PHASE CONCENTRATION (ug/L) -ONE DIMENSION
C      XN     = FRUENDLICH 1/n -FROM HC PROGRAM
C      ZSPOW = SUBROUTINE THE SOLVES THE EQUATIONS
C      ZZ     = VARIABLE USED TO CALCULATE INITIAL Q
C
C
C                    ***PROGRAM***
C
      SUBROUTINE IAST(X,M,NA,F)
C
C                    ***DIMENSIONING***
C
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION DM(50),V(50),Q(10,50),PAR(50),XX(10),CE(50),WK(621)
     $,F(50),X(18),P(18),B(18),CI(7,50),QI(7,50)
      INTEGER D,RES,AA(18)
      DOUBLE PRECISION K,MW
      EXTERNAL FCN
      COMMON /ZSQ/DM,CO,V,K,XN,D,CE,NN,RES,MW,P,AA,B,CI,QI,NC
C
C               ***ENTER THE PARAMETERS FOR ZSPOW***
C
      KO=0
      PAR(1)=K
      PAR(11)=XN
      PAR(21)=CO
C
      IF (AA(1) .EQ. 1) THEN
       PAR(2)=X(1)
      ELSE
       PAR(2)=P(1)
       KO=KO+1
      ENDIF
      IF (AA(2) .EQ. 1) THEN
       PAR(12)=X(2-KO)
      ELSE
       PAR(12)=P(2)
       KO=KO+1
      ENDIF
      IF (AA(3) .EQ. 1) THEN
       PAR(22)=X(3-KO)
      ELSE
       PAR(22)=P(3)
       KO=KO+1
      ENDIF
C
      IF (NN .GE. 2) THEN
       IF (AA(4) .EQ. 1) THEN
        PAR(3)=X(4-KO)
       ELSE
```

```
        PAR(3)=P(4)
        KO=KO+1
       ENDIF
       IF (AA(5) .EQ. 1) THEN
        PAR(13)=X(5-KO)
       ELSE
        PAR(13)=P(5)
        KO=KO+1
       ENDIF
       IF (AA(6) .EQ. 1) THEN
        PAR(23)=X(6-KO)
       ELSE
        PAR(23)=P(6)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .GE. 3) THEN
       IF (AA(7) .EQ. 1) THEN
        PAR(4)=X(7-KO)
       ELSE
        PAR(4)=P(7)
        KO=KO+1
       ENDIF
       IF (AA(8) .EQ. 1) THEN
        PAR(14)=X(8-KO)
       ELSE
        PAR(14)=P(8)
        KO=KO+1
       ENDIF
       IF (AA(9) .EQ. 1) THEN
        PAR(24)=X(9-KO)
       ELSE
        PAR(24)=P(9)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .GE. 4) THEN
       IF (AA(10) .EQ. 1) THEN
        PAR(5)=X(10-KO)
       ELSE
        PAR(5)=P(10)
        KO=KO+1
       ENDIF
       IF (AA(11) .EQ. 1) THEN
        PAR(15)=X(11-KO)
       ELSE
        PAR(15)=P(11)
        KO=KO+1
       ENDIF
       IF (AA(12) .EQ. 1) THEN
        PAR(25)=X(12-KO)
       ELSE
        PAR(25)=P(12)
        KO=KO+1
       ENDIF
      ENDIF
```

```
C
      IF (NN .GE. 5) THEN
       IF (AA(13) .EQ. 1) THEN
        PAR(6)=X(13-KO)
       ELSE
        PAR(6)=P(13)
        KO=KO+1
       ENDIF
       IF (AA(14) .EQ. 1) THEN
        PAR(16)=X(14-KO)
       ELSE
        PAR(16)=P(14)
        KO=KO+1
       ENDIF
       IF (AA(15) .EQ. 1) THEN
        PAR(26)=X(15-KO)
       ELSE
        PAR(26)=P(15)
        KO=KO+1
       ENDIF
      ENDIF
C
      IF (NN .EQ. 6) THEN
       IF (AA(16) .EQ. 1) THEN
        PAR(7)=X(16-KO)
       ELSE
        PAR(7)=P(16)
        KO=KO+1
       ENDIF
       IF (AA(17) .EQ. 1) THEN
        PAR(17)=X(17-KO)
       ELSE
        PAR(17)=P(17)
        KO=KO+1
       ENDIF
       IF (AA(18) .EQ. 1) THEN
        PAR(27)=X(18-KO)
       ELSE
        PAR(27)=P(18)
        KO=KO+1
       ENDIF
      ENDIF
C
C                 ***SOLVE EACH DOSAGE INDIVIDUALLY***
C
      NC=1+NN
      DO 1200 J=1,D
       L=0
       ZZ=0.70D0
       PAR(30)=DM(J)
       PAR(40)=V(J)
C
C                  ***CALCULATE INITIAL GUESSES ON Q'S***
C
 1125  IF (J .EQ. 1) THEN
        DO 1130 I=1,NC
         Q(I,1)=ZZ*PAR(20+I)*V(1)/DM(1)
 1130   CONTINUE
```

```
      ELSE
       DO 1140 I=1,NC
        Q(I,J)=0.50D0*Q(I,J-1)
1140   CONTINUE
      ENDIF
C
C              ***PUT Q INTO ONE DIMENSIONAL FORM***
C
      DO 1145 I=1,NC
       XX(I)=Q(I,J)
1145  CONTINUE
C
C              ***ENTER OTHER PARAMETERS FOR ZSPOW***
C
      NSIGG=4
1152  N=NC
      ITMAX=100
C
C             ***CALL ZSPOW TO SOLVE THE EQUATIONS***
C
      CALL ZSPOW(FCN,NSIGG,N,ITMAX,PAR,XX,FNORM,WK,IER)
C
C                    ***FIX ANY ERRORS***
C
      IF (IER .EQ. 129 .OR. IER .EQ.131) THEN
       IF (L .EQ. 0) THEN
        ZZ=0.50D0
        L=L+1
        GOTO 1125
       ENDIF
       IF (L .EQ. 1) THEN
        ZZ=0.20D0
        L=L+1
        GOTO 1125
       ENDIF
       IF (L .EQ. 2) THEN
        WRITE(7,1155) DM(J)*1000.0D0
1155    FORMAT(1X,'THERE IS AN ERROR WITH INITIAL CONCENTRATION THE',/,
     $1X,'PROGRAMS INTERNAL FIXING ROUTINE DID NOT HELP  DOSAGE=',F10.4)
        ENDIF
      ENDIF
C
      IF (IER .EQ. 130) THEN
       NSIGG=NSIGG-1
     . IF (NSIGG .LT. 0) THEN
        WRITE(7,1160) DM(J)*1000.0D0
1160    FORMAT(1X,'THE NUMBER OF SIGNIFICANT FIGURES HAS DROPPED BELOW
     $ZERO.  THERE ARE NO RESULTS FOR DOSAGE=',F10.4)
        GOTO 1200
       ENDIF
       GOTO 1152
      ENDIF
C
C     ***CALCULATE THE LIQUID CONCENTRATIONS OF COMPONENTS***
C
      DO 1170 I=1,NC
       QI(I,J)=XX(I)
       CI(I,J)=PAR(20+I)-DM(J)/V(J)*QI(I,J)
```

```
 1170   CONTINUE
C
C                    ***SET UP RESIDUALS***
C
        IF (RES .EQ. 0) F(J)=CE(J)-CI(1,J)
        IF (RES .EQ. 1) F(J)=(CE(J)-CI(1,J))/CE(J)
C
 1200 CONTINUE
C
C             ***SET B TO FINAL PARAMETER VALUES***
C
      B(1)=PAR(2)
      B(2)=PAR(12)
      B(3)=PAR(22)
      IF (NN .GE. 2) THEN
       B(4)=PAR(3)
       B(5)=PAR(13)
       B(6)=PAR(23)
      ENDIF
      IF (NN .GE. 3) THEN
       B(7)=PAR(4)
       B(8)=PAR(14)
       B(9)=PAR(24)
      ENDIF
      IF (NN .GE. 4) THEN
       B(10)=PAR(5)
       B(11)=PAR(15)
       B(12)=PAR(25)
      ENDIF
      IF (NN .GE. 5) THEN
       B(13)=PAR(6)
       B(14)=PAR(16)
       B(15)=PAR(26)
      ENDIF
      IF (NN .EQ. 6) THEN
       B(16)=PAR(7)
       B(17)=PAR(17)
       B(18)=PAR(27)
      ENDIF
C
C                   ***PRINT TO SCREEN***
C

C      PRINT*, '           C(1)                      C(D/2)
C     $        C(D)'
C      PRINT*, CI(1,1)*MW,CI(1,D/2)*MW,CI(1,D)*MW
      RETURN
      END
C
C
C                 *******SUBROUTINE FCN*******
C
C      THIS SUBROUTINE WILL SET UP THE EQUATIONS THAT WILL BE USED IN
C     THE ZSPOW SUBROUTINE.
C
      SUBROUTINE FCN(XX,F,N,PAR)
C
      DOUBLE PRECISION XX(N),F(N),PAR(50),QNQ,QT
      INTEGER I,N
      QT=0.0D0
      QNQ=0.0D0
      DO 1510 I=1,N
       QT=QT+XX(I)
       QNQ=QNQ+PAR(10+I)*XX(I)
 1510 CONTINUE
      DO 1520 I=1,N
       F(I)=PAR(20+I)-PAR(30)/PAR(40)*XX(I)-XX(I)/QT*(QNQ/PAR(10+I)/
     $PAR(I))**PAR(10+I)
 1520 CONTINUE
      RETURN
      END
```

```
C
C       **************************************************
C       *                                                *
C       *        EQUILIBRIUM THEORY CALCULATIONS         *
C       *                                                *
C       **************************************************
C
C
C       CREATED BY :
C        PAUL LUFT             :  GRADUATE STUDENT, CHEM ENG
C        DAVID HAND            :  ASSIS. RESEARCH ENG., WATER
C                                 AND WASTE MNGE. PROGRAM
C        DR. JOHN CRITTENDEN :  PROF. CIVIL ENG.
C              MICHIGAN TECHNOLOGICAL UNIVERSITY
C                    HOUGHTON, MI  49931
C
C       THIS PROGRAM CALCULATES MULTICOMPONENT BREAKTHROUGH
C       FOR FIXED BED ADSORBERS, ASSUMING NO MASS TRANSFER
C       RESISTANCES.  THE LIQUID AND SOLID PHASE CONCENTRATIONS
C       FOR EACH COMPONENT IN EACH ZONE ARE CALCULATED. THE
C       VELOCITY OF EACH WAVE IS CALCULATED.  IDEAL ADSORBED
C       SOLUTION THEORY IS USED TO PREDICT COMPETITION.
C
C
C       NOTE: THIS VERSION REVISED MARCH 9,1988 BY
C             R.C.ANDREWS TO ALLOW INPUT DATA TO BE
C             READ IN TERMS OF UG INSTEAD OF UM.
C
C       OUTPUT DATA IS PRINTED IN TWO FORMATS:
C             (1) ug
C             (2) um
C
C
C       INPUT
C       N      : NUMBER OF COMPONENTS
C       CO     : ARRAY OF INITIAL CONCENTRATIONS (UG/L)
C       EPP    : BED VOID FRACTION
C       RHOB   : BULK DENSITY OF ADSORBATE (G/CM**3)
C       FLRT   : FLOW RATE (GPM/FT**2)
C       XK     : ARRAY OF FREUNDLICH K'S (UG/G)(L/UG)**1/N
C       XN     : ARRAY OF FREUNDLICH 1/N'S
C       WM     : MOLECULAR WEIGHT
C       NOTE:    WHEN USING HC'S (UM) AS INPUT, WM MUST ALWAYS
C                BE 1.0.
C
      DIMENSION  BVF(40),DG(40,40),QAVE(40,40)
      COMMON XK(40),XN(40),C(40,40),Q(40,40),N,I,RHOB,EPP,
     + VF,VW(40),CO(40),CSO(40,40),WM(40),COK(40),TESTK(40),
     + CONV(40),XKK(40),CON(40),W(40),TESTCV(40),TESTWM(40)
C
C.....READ IN THE DATA
C
      READ(4,*) N,EPP,RHOB,FLRT
      READ(4,*) (CO(I),XK(I),XN(I),WM(I),I=1,N)
      DO 79, I=1,N
   79 CONTINUE
C
C     CONVERT INPUT DATA FROM UM TO UG.
```

```
C
      DO 80, I=1,N
      CONV(I)=0
      CO(I)=CO(I)/WM(I)
      CONV(I)=(WM(I)*(1/(WM(I)**(XN(I)))))
      TESTCV(I)=CONV(I)
      XK(I)=XK(I)*(1/CONV(I))
      TESTK(I)=XK(I)
      TESTWM(I)=WM(I)
   80 CONTINUE
      DO 82, K=1,N
      COK(K)=CO(K)*WM(K)
      XKK(K)=XK(K)*CONV(K)
   82 CONTINUE
C
      VF = FLRT*0.06791/EPP
         RHOB = RHOB*1000
      EPS = 1.0E-6*CO(1)
C
C.....IN FIRST ZONE SET ALL THE CONCENTRATIONS TO CO
C
      DO 30 J=1,N
       XN(J) = 1/XN(J)
       VW(J) = 0.0
  30  C(J,1) = CO(J)
C
C.....CALL SUBROUTINE IAS TO GET Q'S IN ZONE 1
C
      CALL IAS(1)
        I = 1
        GO TO 35
C
C.....DO ZONE BY ZONE CALCULATIONS FOR VELOCITY OF WAVE AND OVERSHOOT
C.....CONCENTRATIONS
C
   55 DO 40 I=2,N+1
      SUM = 0.0
C
C.....CALCULATE VELOCITY OF WAVE I-1
C
         IF(I.GT.2) THEN
         SUM = (Q(I-1,1)*RHOB+EPP*C(I-1,1))*VW(1)
      DO 50 J=2,I-2
  50  SUM = SUM +(Q(I-1,J)*RHOB+EPP*C(I-1,J))*(VW(J)-VW(J-1))
         ENDIF
       IF(I .EQ. 2) THEN
       XXX = 0.0
       ELSE
       XXX = VW(I-2)
       ENDIF
      VW(I-1) = (EPP*VF*CO(I-1) - SUM +(Q(I-1,I-1)*RHOB+EPP*C(I-1,I-1))
     +  *XXX)/(Q(I-1,I-1)*RHOB+EPP*C(I-1,I-1))
      IF(I .EQ. N+1) GO TO 40
C
C.....USE SUBROUTINE IAS TO CALCULATE THE OVERSHOOT CONCENTRATION
C
          CALL IAS(I)
C
```

```
C.....DETERMINE STRONGEST COMPONENT IN ZONE I
C
   35 DGX = 0.0
      DO 45 J=I,N
      DGY = RHOB*Q(J,I)/(C(J,I)*EPP)
      IF(DGY .GT. DGX) THEN
      DGX = DGY
      IX = J
      ENDIF
   45 CONTINUE
      XXK = XK(IX)
      XK(IX) = XK(I)
      XK(I) = XXK
      XXN = XN(IX)
      XN(IX) = XN(I)
      XN(I) = XXN
      XCO = CO(IX)
      CO(IX) = CO(I)
      CO(I) = XCO
      DO 65 K=1,I
      XC = C(IX,K)
      C(IX,K) = C(I,K)
      C(I,K) = XC
      XQ = Q(IX,K)
      Q(IX,K) = Q(I,K)
   65 Q(I,K) = XQ
      IF(I .EQ. 1) GO TO 55
   40 CONTINUE
C
C.....CALCULATE BED VOLUMES FED
C
      DO 60 I=1,N
      SUM = (Q(I,1)*RHOB+C(I,1)*EPP)*VW(1)
      DO 70 J=2,I
   70 SUM = SUM + (Q(I,J)*RHOB+C(I,J)*EPP)*(VW(J)-VW(J-1))
   60 BVF(I) = SUM/(CO(I)*VW(I))
C
C.....CALCULATE DG'S
C
      DO 91 I=1,N
      DO 90 J=1,N
      IF(C(I,J) .EQ. 0.0) THEN
      DG(I,J) = 0.0
      GO TO 80
      ENDIF
   90 DG(I,J) = RHOB*Q(I,J)/(C(I,J)*EPP)
   91 CONTINUE
C
C.....CALCULATE Q AVERAGE FOR EACH ZONE
C
      DO 130 J=1,N
  130 QAVE(J,1) = Q(J,1)
      DO 140 J=1,N
      DO 150 I=2,N
  150 QAVE(J,I) = (QAVE(J,I-1)*VW(I-1)+Q(J,I)*(VW(I)-VW(I-1)))/VW(I)
  140 CONTINUE
C
C.....PRINT RESULTS
```

```
C
      WRITE(7,*) 'EQUILIBRIUM THEORY CALCULATIONS'
      WRITE(7,1000) N,EPP,RHOB/1000,FLRT
 1000 FORMAT(//,T10,'NUMBER OF COMPONENTS :',T50,I2,/,
     + T10,'BED VOID FRACTION :',T51,F5.3,/,T10,
     + 'BULK DENSITY OF ADSORBATE (G/CM**3) :',T46,F10.3,/,T10,
     + 'FLOWRATE  (GPM/FT**2) :                ',T46,F10.3,//)
      WRITE(7,1001)
 1001 FORMAT(T21,'BED VOLUMES FED',T39,'VELOCITY OF WAVE',
     +  T57,'TREATMENT CAPACITY',/,T21,'TO BREAKTHROUGH',T43,
     +  '(CM/SEC)',T57,'(MG CARBON/L WATER)',/)
      DO 100 I=1,N
 100  WRITE(7,1002) I,BVF(I),VW(I),RHOB*1000/BVF(I)
 1002 FORMAT(T8,'ZONE(',T13,I2,T15,')',T17,F15.1,T39,E15.8,T55,F15.4)
      DO 110 I=1,N
      IF(I .EQ. 1) THEN
      ZZZ = 0.0
      ELSE
      ZZZ = VW(I-1)/VW(N)
      ENDIF
      WRITE(7,1003) I,XK(I),1/XN(I),1000*CO(I)**(1-1/XN(I))/XK(I)
     +  ,I,VW(I)/VW(N)-ZZZ
 1003 FORMAT(//,'COMPONENT(',T11,I2,T13,')',//,T10,
     + 'FREUNDLICH K(UM/G)(L/UM)**1/N :',T45,F10.2,/,T10,
     + 'FREUNDLICH 1/N :',T45,F10.4,/,T10,
     + 'SINGLE SOLUTE TREATMENT CAPACITY',/,T12,
     + '(MG CARBON/L WATER) :',T40,F15.4,/,T10,
     + 'DIMENSIONLESS BED LENGTH',/,T12,
     + 'FOR ZONE(',T21,I2,T23,') :',T45,F10.8,//,T22,
     + 'C(UM/L)',T39,'Q(UM/G)',T52,'C/CO',T66,'DG',T80,'QAVE')
      DO 120 J=1,I
 120  WRITE(7,1004) J,C(I,J),Q(I,J),C(I,J)/CO(I),DG(I,J),QAVE(I,J)
 1004 FORMAT(T5,'ZONE(',T10,I2,T12,')',T13,F15.3,T31,F15.3,
     + T51,F7.4,T57,F15.3,T75,F10.3)
 110  CONTINUE
C
       DO 1173 I=1,N
       DO 1172 J=1,N
       IF(XK(I) .EQ. TESTK(J)) THEN
       CONV(I)=TESTCV(J)
       WM(I)=TESTWM(J)
       ENDIF
 1172  CONTINUE
 1173  CONTINUE
C
      WRITE(7,1109)
 1109 FORMAT(//////,'EQUILIBRIUM THEORY CALCULATIONS-
     +  OUTPUT DATA CONVERTED TO MASS BASIS  i.e UG/L')
      WRITE(7,1110) N,EPP,RHOB/1000,FLRT
 1110 FORMAT(//,T10,'NUMBER OF COMPONENTS :',T50,I2,/,
     + T10,'BED VOID FRACTION :',T51,F5.3,/,T10,
     + 'BULK DENSITY OF ADSORBATE (G/CM**3) :',T46,F10.3,/,T10,
     + 'FLOWRATE  (GPM/FT**2) :                ',T46,F10.3,//)
      WRITE(7,1121)
 1121 FORMAT(T21,'BED VOLUMES FED',T39,'VELOCITY OF WAVE',
     +  T57,'TREATMENT CAPACITY',/,T21,'TO BREAKTHROUGH',T43,
     +  '(CM/SEC)',T57,'(MG CARBON/L WATER)',/)
      DO 141 I=1,N
```

```
  141  WRITE(7,1132) I,BVF(I).VW(I).RHOB*1000/BVF(I)
 1132 FORMAT(T8,'ZONE(',T13,I2,T15,')',T17,F15.1,T39,E15.8,T55,F15.4)
       DO 111 I=1,N
       IF(I .EQ. 1) THEN
       ZZZ = 0.0
       ELSE
       ZZZ = VW(I-1)/VW(N)
       ENDIF
       WRITE(7,1143) I,XK(I)*CONV(I),1/XN(I),
     +  1000*CO(I)**(1-1/XN(I))/XK(I)
     +  ,I,VW(I)/VW(N)-ZZZ
 1143 FORMAT(//,'COMPONENT(',T11,I2,T13,')',//,T10,
     + 'FREUNDLICH K(UG/G)(L/UG)**1/N :',T45,F10.2,/,T10,
     + 'FREUNDLICH 1/N :',T45,F10.4,/,T10,
     + 'SINGLE SOLUTE TREATMENT CAPACITY',/,T12,
     + '(MG CARBON/L WATER) :',T40,F15.4,/,T10,
     + 'DIMENSIONLESS BED LENGTH',/,T12,
     + 'FOR ZONE(',T21,I2,T23,') :',T45,F10.8,//,T22,
     + 'C(UG/L)',T39,'Q(UG/G)',T52,'C/CO',T66,'DG',T80,'QAVE')
      DO 142 J=1,I
  142 WRITE(7,1144) J,C(I,J)*WM(I),Q(I,J)*WM(I),C(I,J)/CO(I),DG(I,J)
 1144 FORMAT(T5,'ZONE(',T10,I2,T12,')',T13,F15.3,T31,F15.3,
     + T51,F7.4,T57,F15.3,T75,F10.3)
  111 CONTINUE
      WRITE(7,1145)
 1145 FORMAT(///,'END PROGRAM EXECUTION',/)
C
C
      FIRST=0
      DO 191 J=N,1,-1
      DO 192 I=J,1,-1
      IF (I .EQ. J) THEN
      WRITE(6,184) BVF(I),FIRST
      ENDIF
      IF (I .LT. J) THEN
      WRITE(6,184) BVF(I),C(J,I+1)/CO(J)
      ENDIF
      WRITE(6,184) BVF(I),C(J,I)/CO(J)
      XBVF=BVF(I)*1.10
      XCO=C(J,I)/CO(J)
  192 CONTINUE
      WRITE(6,184) XBVF,XCO
  184 FORMAT(' ',F15.4,F7.4)
  191 CONTINUE
C
C
      STOP
C      DEBUG INIT,SUBTRACE
      END
C
C
C
C
      SUBROUTINE IAS(I)
C
C
      DIMENSION A(80,80),X(80)
      COMMON XK(40),XN(40),C(40,40),Q(40,40),N,LL,RHOB,EPP,
     + VF,VW(40),CO(40),CSO(40,40)
C
C.....GET INITIAL GUESSES ON Q'S
C
      EPS = 1.E-4
 15   RATIO = 0.25
      RAT = 0.25
 10   IF(I .EQ. 1) THEN
      DO 25 J=2,N
 25   Q(J,I) = RATIO*XK(J)*C(J,I)**(1/XN(J))
      ELSE
      DO 11 J=I+1,N
 11   Q(J,I) = RATIO*Q(J,I-1)
      ENDIF
      Q(I,I) = RAT*XK(I)*CO(I)**(1/XN(I))
C
C.....INITIALIZE F(ITERATION COUNT), EPS(ERROR CRITERIA), XNQ, AND QT
C
       F = 0.0
 20    XNQ = 0.0
       QT = 0.0
C
C.....CALCULATE XNQ AND QT
C
       DO 30 J=I,N
       XNQ = XNQ + XN(J)*Q(J,I)
 30    QT = QT + Q(J,I)
C
C..... SET UP THE JACOBIAN
C
       DO 50 K=I,N
       Z = Q(K,I)*((XNQ/(XK(K)*XN(K)))**XN(K))/QT
      IF(I .EQ. 1) THEN
      ZX = 0.0
      ELSE
        ZX = RHOB*VW(I-1)/VF/((1-VW(I-1)/VF)*EPP)
      ENDIF
       DO 40 J=I,N
       A(K-I+1,J-I+1) = Z/QT-XN(K)*XN(J)*Z/XNQ
 40    IF(K .EQ. J) A(K-I+1,K-I+1) = A(K-I+1,K-I+1)-Z/Q(K,I)+ZX
      IF(I .GT. 1) THEN
      A(K-I+1,N-I+2) = -C(K,I-1) + Z - ZX*(Q(K,I)-Q(K,I-1))
      ELSE
      A(K-I+1,N-I+2) = -C(K,I) + Z
      ENDIF
 50   CONTINUE
C
C.....CALL SUBROUTINE SIMUL TO SOLVE THE AUGMENTED JACOBIAN
C
      CALL SIMUL(N-I+1,A,X,1.E-8,0,80,DETER)
C
C.....COUNT ITERATIONS
C
      F = F + 1.0
      IF(F .GT. 10.0) THEN
      RAT = RAT + 0.25
      IF(RAT .GT. 40.0) THEN
      RAT = 0.25
```

```
            RATIO = RATIO + 0.25
            IF(RATIO .GT. 20.0) GO TO 999
            ENDIF
            GO TO 10
            ENDIF
C
C.....CHECK FOR CONVERGENCE
C
            DO 70 J=1,N+1-I
            IF(ABS(X(J)) .LT. EPS) GO TO 70
C
C.....IF DIDN'T CONVERGE CHANGE Q'S AND REITERATE
C
            DO 60 K=I,N
            Q(K,I) = Q(K,I) + X(K-I+1)
   60        IF(Q(K,I) .LE. 0.0) Q(K,I) = 0.00001
            GO TO 20
   70       CONTINUE
C
C.....CALCULATE LIQUID PHASE CONCENTRATIONS
C
              DO 75 J=I,N
              C(J,I) = Q(J,I)*(XNQ/(XN(J)*XK(J)))**XN(J)/QT
            CSO(J,I) = C(J,I)*(Q(J,I)/(QT))
   75       CONTINUE
C
            IF(I.GT.1) THEN
            DO 77 J=I,N
            C(J,I+1) = (Q(J,I+1) - Q(J,I))*RHOB*VW(I)/((1.-VW(I)/VF)
           +*VF*EPP) + C(J,I)
    77      CONTINUE
            ELSE
            ENDIF
C.....CHECK IF IAS EQUATIONS ARE SATISFIED
C
            DO 80 K=I,N
            ERR = 1-Q(K,I)*(XNQ/(XN(K)*XK(K)))**XN(K)/(QT*C(K,I))
             IF(I .GT. 1) THEN
            ERR = 1-((Q(K,I)-Q(K,I-1))*RHOB*VW(I-1)/(VF*EPP*(1-VW(I-1)/
           + VF))+C(K,I-1))/(Q(K,I)*(XNQ/(XN(K)*XK(K)))**XN(K)/QT)
            ENDIF
            IF(ABS(ERR) .GT. 0.001) THEN
            EPS = 0.1*EPS
            IF(EPS .LT. 1.E-6*C(K,I)) GO TO 80
            GO TO 15
            ENDIF
   80       CONTINUE
            RETURN
  999       WRITE(7,*) 'SUBROUTINE IAS FAILED TO CONVERGE AT ZONE',I
            RETURN
C           DEBUG INIT,SUBTRACE
            END
C
C
C
C
C************************SUBROUTINE SIMUL*******************************
C
```

```
C        THIS PROGRAM WAS TAKEN FROM CARNAHAN, LUTHER, AND WILKES,
C        'APPLIED NUMERICAL METHODS,' WILEY, NEW YORK, 1969, P290-291
C        IT WAS MODIFIED FROM DOUBLE PRECISION TO SINGLE PRECISION
C        AND CONVERTED FROM A FUNCTION TO A SUBROUTINE BY J. ORAVITZ
C
      SUBROUTINE SIMUL(N,A,X,EPS,INDIC,NRC,DETER)
C
C        WHEN INDIC IS NEGATIVE, SIMUL COMPUTES THE INVERSE OF THE N BY
C        N MATRIX A IN PLACQ.  WHEN INDIC IS ZERO, SIMUL COMPUTES THE
C        N SOLUTIONS X(1)...X(N) CORRESPONDING TO THE SET OF LINEAR
C        EQUATIONS WITH AUGMENTED MATRIX OF COEFFICIENTS IN THE N BY
C        N+1 ARRAY A NAD IN ADDITION COMPUTES THE INVERSE OF THE
C        COEFFICIENT MATRIX IN PLACE AS ABOVE.  IF INDIC IS POSITIVE,
C        THE SET OF LINEAR EQUATIONS IS SOLVED BUT THE INVERSE IS NOT
C        COMPUTED IN PLACE.  THE GAUSS-JORDAN COMPLETE ELIMINATION METHOD
C        IS EMPLOYED WITH THE MAXIMUM PIVOT STRATEGY.  ROW AND COLUMN
C        SUBSCRIPTS OF SUCCESSIVE PIVOT ELEMENTS ARE SAVED IN ORDER IN
C        THE IROW AND JCOL ARRAYS RESPECTIVELY.  K IS THE PIVOT COUNTER,
C        PIVOT THE ALGEBRAIC VALUE OF THE PIVOT ELEMENT, MAX
C        THE NUMBER OF COLUMNS IN A AND DETER THE DETERMINANT OF THE
C        COEFFICIENT MATRIX.  THE SOLUTIONS ARE COMPUTED IN THE (N+1)TH
C        COLUMN OF A AND THEN UNSCRAMBLED AND PUT IN PROPER ORDER IN
C        X(1)...X(N) USING THE PIVOT SUBSCRIPT INFORMATION AVAILABLE
C        IN THE IROW AND JCOL ARRAYS.  THE SIGN OF THE DETERMINANT IS
C        ADJUSTED, IF NECESSARY, BY DETERMINING IF AN ODD OR EVEN NUMBER
C        OF PAIRWISE INTERCHANGES IS REQUIRED TO PUT THE ELEMENTS OF THE
C        JORD ARRAY IN ASCENDING SEQUENCE WHERE JORD(IROW(I)) = JCOL(I)
C        IF THE INVERSE IS REQUIRED, IT IS UNSCRAMBLED IN PLACE USING
C        Y(1)...Y(N) AS TEMPORARY STORAGE.  THE VALUE OF THE DETERMINANT
C        IS RETURNED AS THE VALUE OF THE FUNCTION.  SHOULD THE POTENTIAL
C        PIVOT OF LORGEST MAGNITUDE BE SMALLER IN MAGNITUDE THAN EPS,
C        THE MATRIX IS CONSIDERED TO BE SINGULAR AND A TRUE ZERO IS
C        RETURNED AS THE VALUE OF THE FUNCTION.
C
      DIMENSION IROW(80),JCOL(80), JORD(80), Y(80), A(NRC,NRC), X(N)
C
      MAX = N
      IF ( INDIC.GE.0 )   MAX = N + 1
C
C     .....IS N LARGER THAN 80 .....
      IF ( N.LE.80 )   GO TO 5
      WRITE (6,200)
      DETER = 0.
      RETURN
C
C     ..... BEGIN ELIMINATION PROCEDURE .....
    5 DETER = 1.
      DO 18   K = 1, N
      KM1 = K - 1
C
C     ..... SEARCH FOR THE PIVOT ELEMENT .....
      PIVOT = 0.
      DO 11   I = 1, N
      DO 11   J = 1, N
C     ..... SCAN IROW AND JCOL ARRAYS FOR INVALID PIVOT SUBSCRIPTS .....
      IF ( K.EQ.1 )   GO TO 9
      DO 8    ISCAN = 1, KM1
      DO 8    JSCAN = 1, KM1
      IF ( I.EQ.IROW(ISCAN) )   GO TO 11
      IF ( J.EQ.JCOL(JSCAN) )   GO TO 11
    8 CONTINUE
    9 IF (ABS(A(I,J)).LE.ABS(PIVOT) )   GO TO 11
      PIVOT = A(I,J)
      IROW(K) = I
      JCOL(K) = J
   11 CONTINUE
C
C     ..... INSURE THAT SELECTED PIVOT IS LARGER THAN EPS ....
      IF ( ABS(PIVOT).GT.EPS )   GO TO 13
      DETER = O.
      RETURN
C
C     ..... UPDATE THE DETERMENANT VALUE .....
   13 IROWK = IROW(K)
      JCOLK = JCOL(K)
      DETER = DETER*PIVOT
C
C     ..... NORMALIZE PIVOT ROW ELEMENTS .....
      DO 14   J = 1,MAX
   14 A(IROWK,J) = A(IROWK,J)/PIVOT
C
C     ..... CARRY OUT ELIMINATION AND DEVELOP INVERSE .....
      A(IROWK,JCOLK) = 1./PIVOT
      DO 18   I = 1,N
      AIJCK = A(I,JCOLK)
      IF ( I.EQ.IROWK )   GO TO 18
      A(I,JCOLK) = - AIJCK/PIVOT
      DO 17   J = 1, MAX
   17  IF ( J.NE.JCOLK )   A(I,J) = A(I,J) - AIJCK*A(IROWK,J)
   18 CONTINUE
C
C     ..... ORDER SOLUTION VALUES (IF AND) AND CREATE JORD ARRAY .....
      DO 20   I = 1, N
      IROWI = IROW(I)
      JCOLI = JCOL(I)
      JORD(IROWI) = JCOLI
   20 IF ( INDIC.GE.O )   X(JCOLI) = A(IROWI,MAX)
C
C     ..... ADJUST SIGN OF DETERMINANT .....
      INTCH = O
      NM1 = N - 1
      DO 22   I = 1, NM1
      IP1 = I + 1
      DO 22   J = IP1, N
      IF ( JORD(J).GE.JORD(I) )   GO TO 22
      JTEMP = JORD(J)
      JORD(J) = JORD(I)
      JORD(I) = JTEMP
      INTCH = INTCH + 1
   22 CONTINUE
      IF ( INTCH/2*2.NE.INTCH )   DETER = - DETER
C
C     ..... IF INDIC IS POSITIVE RETURN WITH RESULTS .....
      IF ( INDIC.LE.O )   GO TO 26
      RETURN
C
```

```
C     ..... IF INDIC IS NEGATIVE OR ZERO, UNSCRAMBLE THE INVERSE
C           FIRST BY ROWS .....
   26 DO 28   J = 1, N
      DO 27   I = 1, N
      IROWI = IROW(I)
      JCOLI = JCOL(I)
   27 Y(JCOLI) = A(IROWI,J)
      DO 28   I = 1, N
   28 A(I,J) = Y(I)
C     .....  THEN BY COLUMNS .....
      DO 30   I = 1, N
      DO 29   J = 1, N
      IROWJ = IROW(J)
      JCOLJ = JCOL(J)
   29 Y(IROWJ) = A(I,JCOLJ)
      DO 30   J = 1, N
   30 A(I,J) = Y(J)
C
C     ..... RETURM FOR INDIC NEGATIVE OR ZERO .....
      RETURN
C
C     ..... FORMAT FOR OUTPUT STATEMENT .....
  200 FORMAT( 10HON TOO BIG )
C
      END
```

Appendix V

IAST Predictions

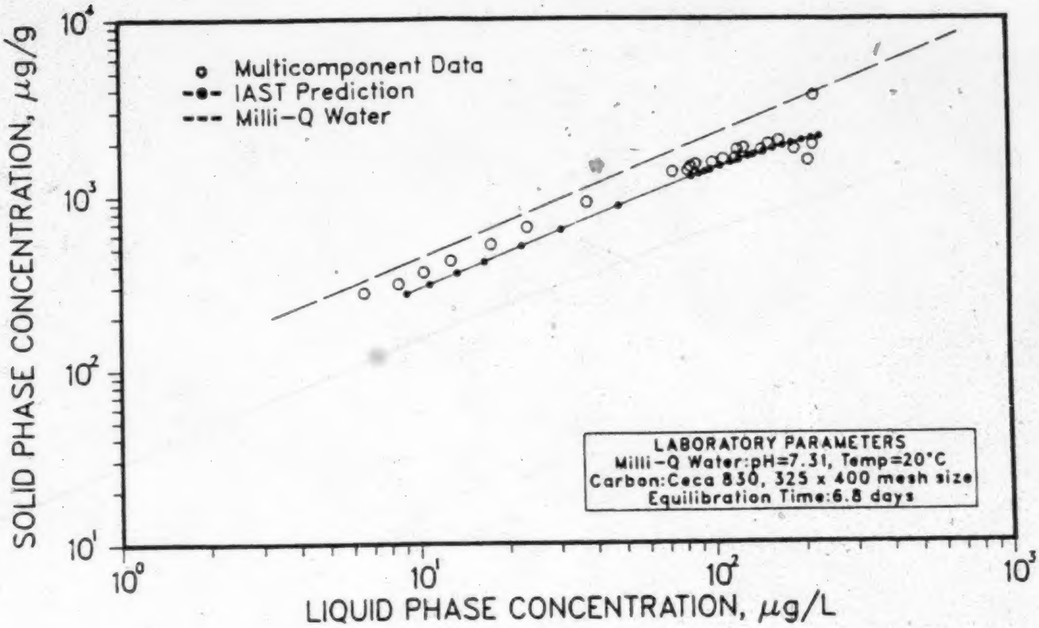


Figure V.1 IAST Prediction and Experimental Data for Chloroform on Ceca 830 in a Two Component Mixture

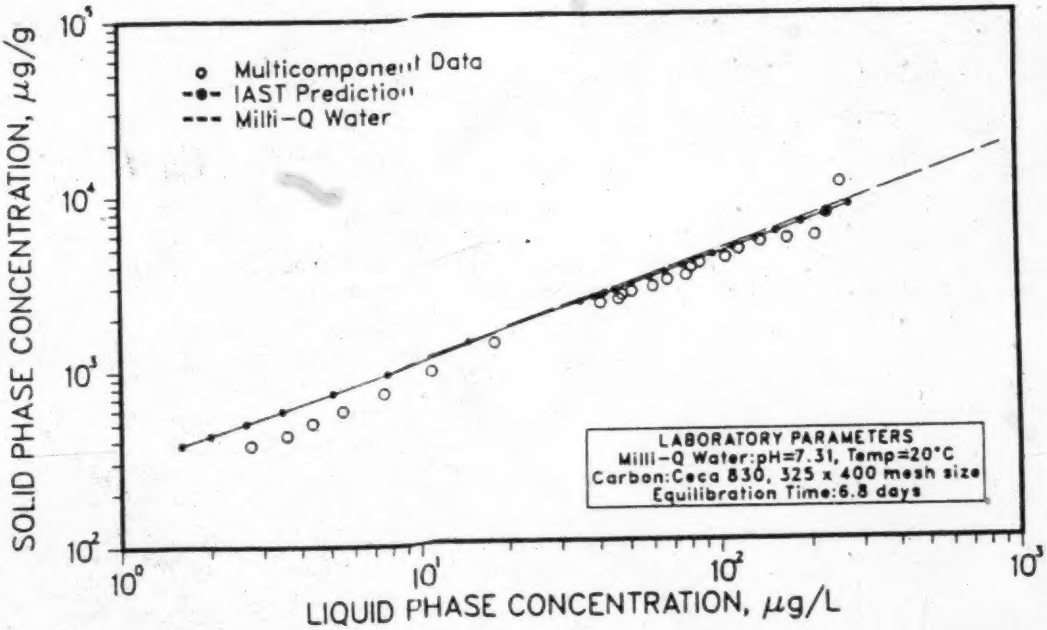


Figure V.2 IAST Prediction and Experimental Data for Bromodichloromethane on Ceca 830 in a Two Component Mixture

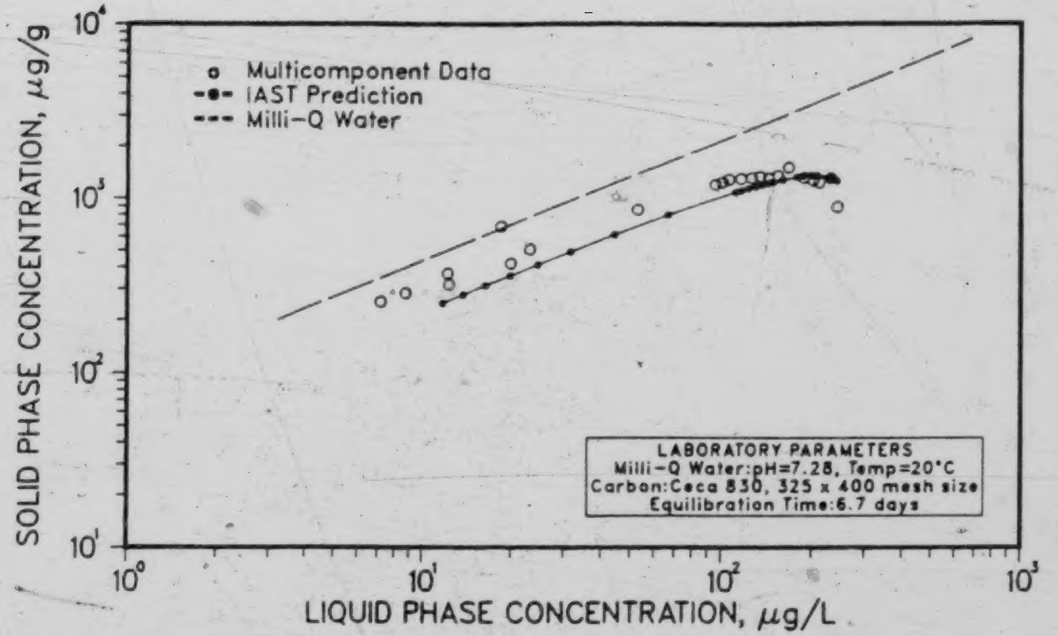


Figure V.3 IAST Prediction and Experimental Data for Chloroform on Ceca 830 in a Four Component Mixture

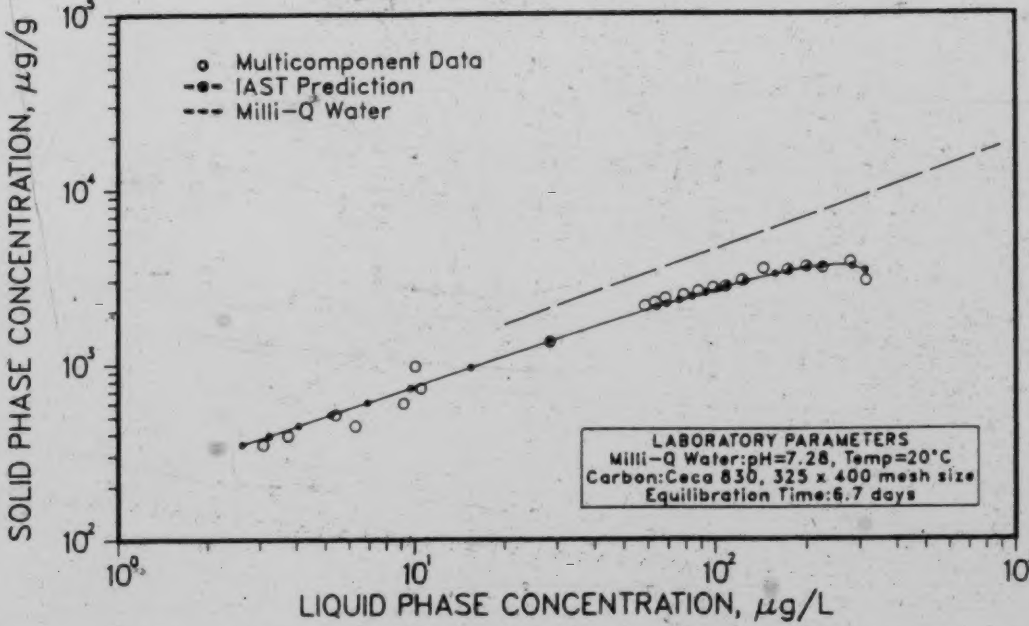


Figure V.4 IAST Prediction and Experimental Data for Bromodichloromethane on Ceca 830 in a Four Component Mixture

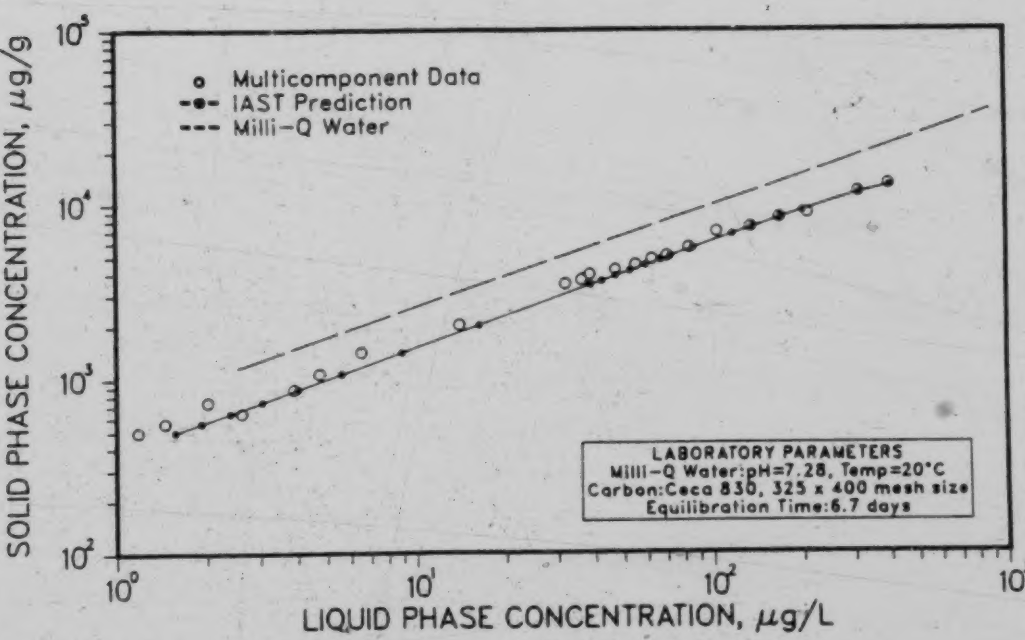


Figure V.5 IAST Prediction and Experimental Data for Dibromochloromethane on Ceca 830 in a Four Component Mixture

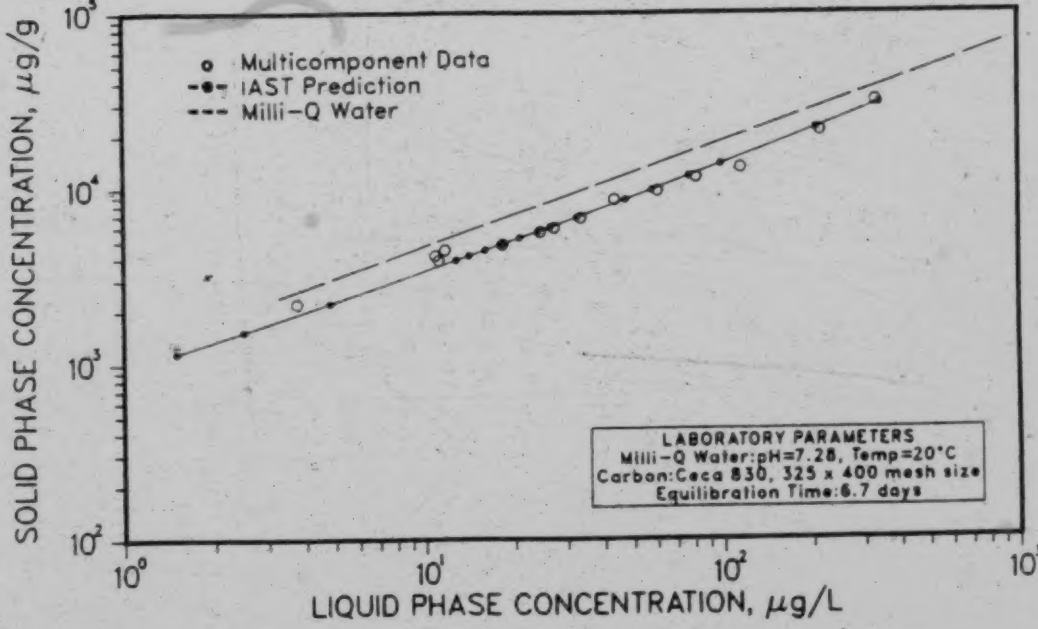


Figure V.6 IAST Prediction and Experimental Data for Bromoform on Ceca 830 in a Four Component Mixture

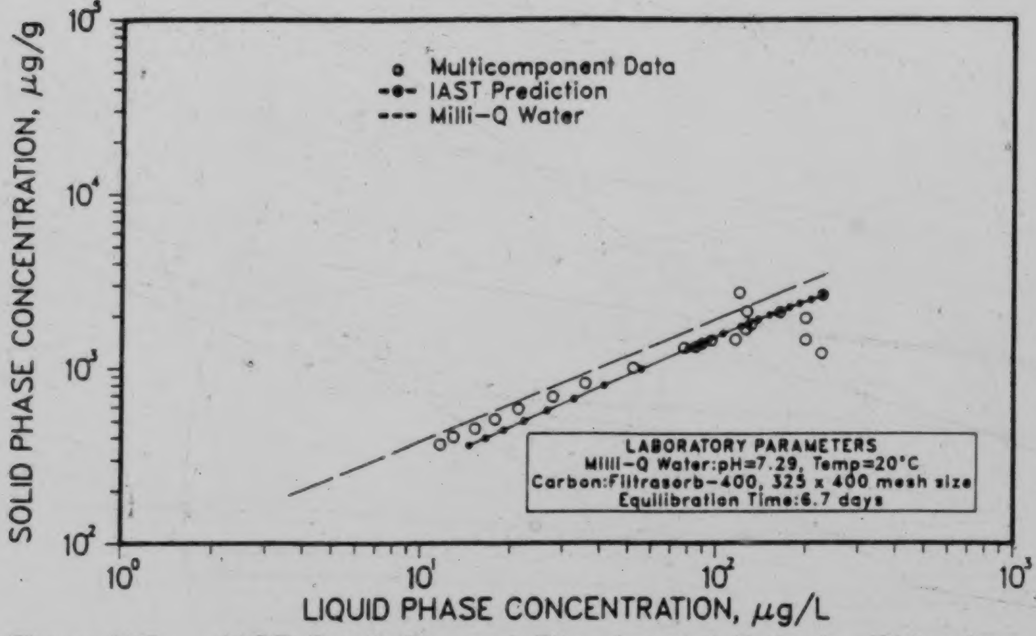


Figure V.7 IAST Prediction and Experimental Data for Chloroform on F-400 in a Two Component Mixture

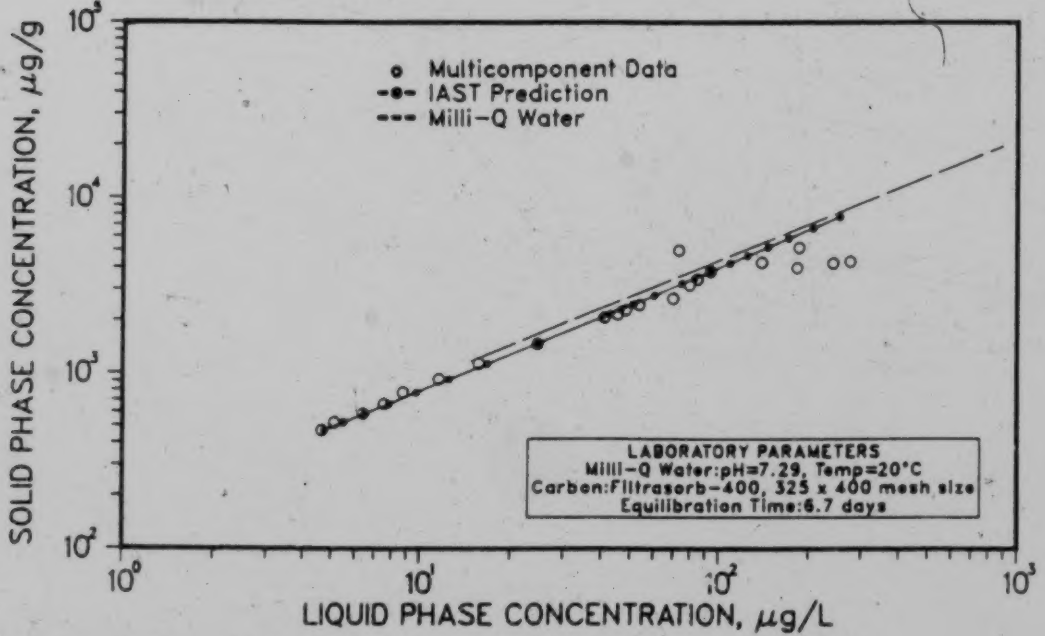


Figure V.8 IAST Prediction and Experimental Data for Bromodichloromethane on F-400 in a Two Component Mixture

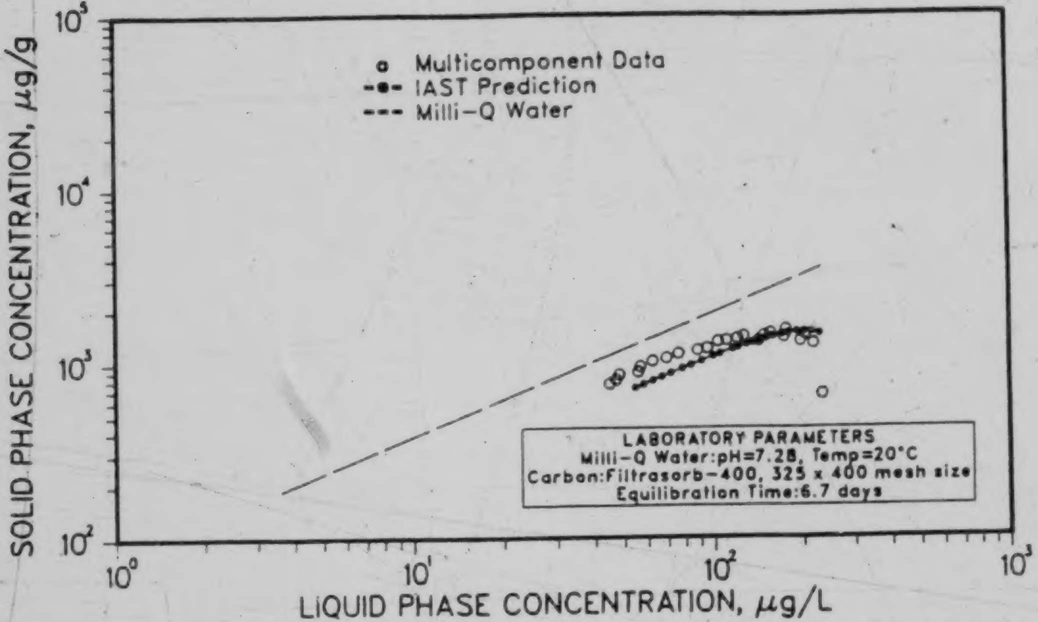


Figure V.9 IAST Prediction and Experimental Data for Chloroform on F-400 in a Four Component Mixture

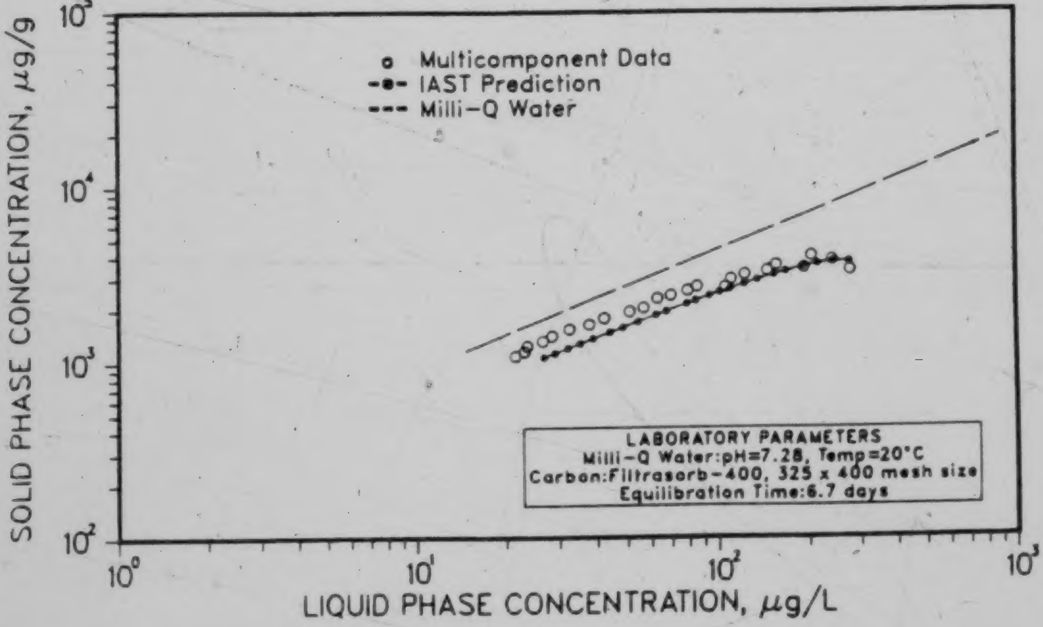


Figure V.10 IAST Prediction and Experimental Data for Bromodichloromethane on F-400 in a Four Component Mixture

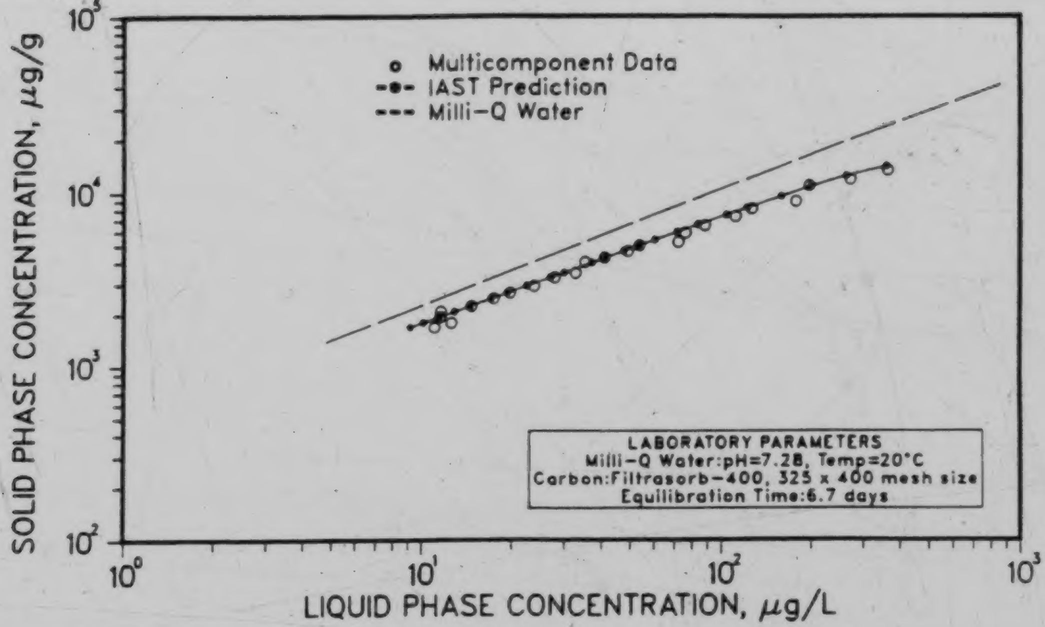


Figure V.11 IAST Prediction and Experimental Data for Dibromochloromethane on F-400 in a Four Component Mixture

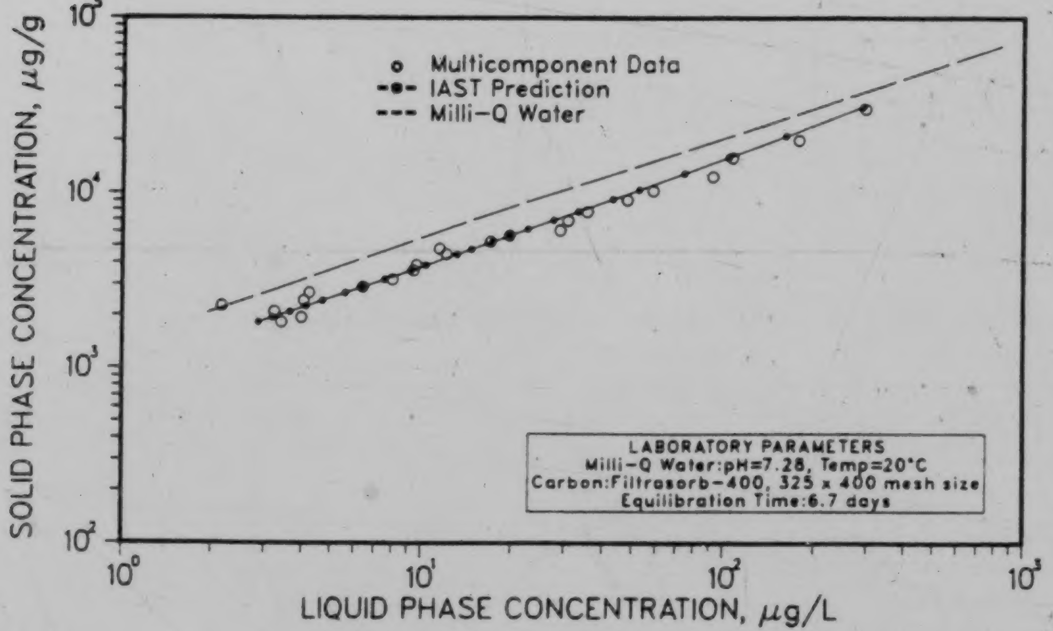


Figure V.12 IAST Prediction and Experimental Data for Bromoform on F-400 in a Four Component Mixture

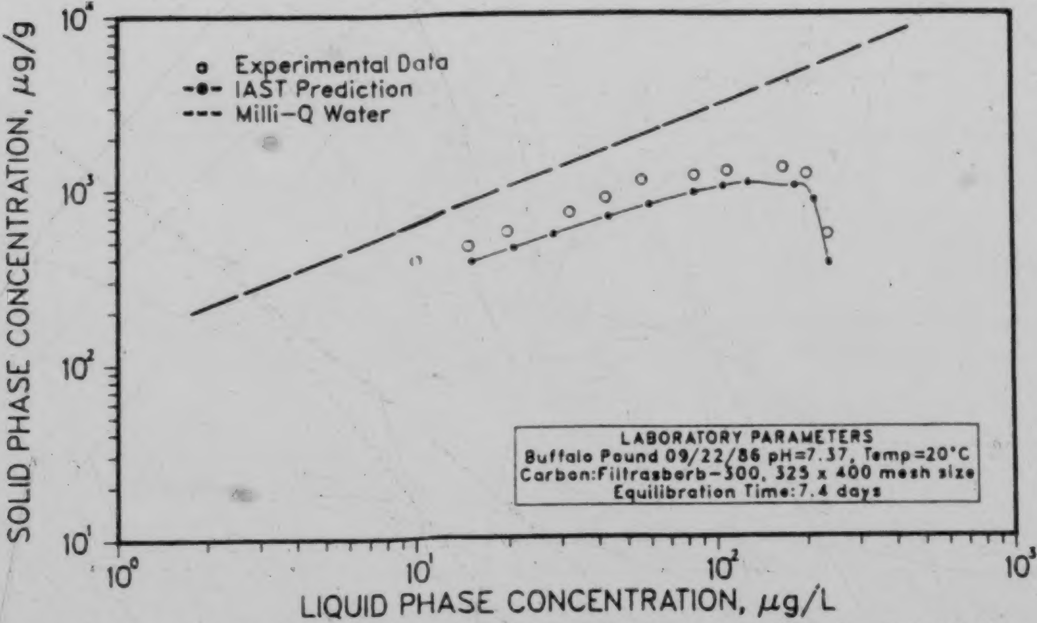


Figure V.13 IAST Prediction for Chloroform on F-300 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

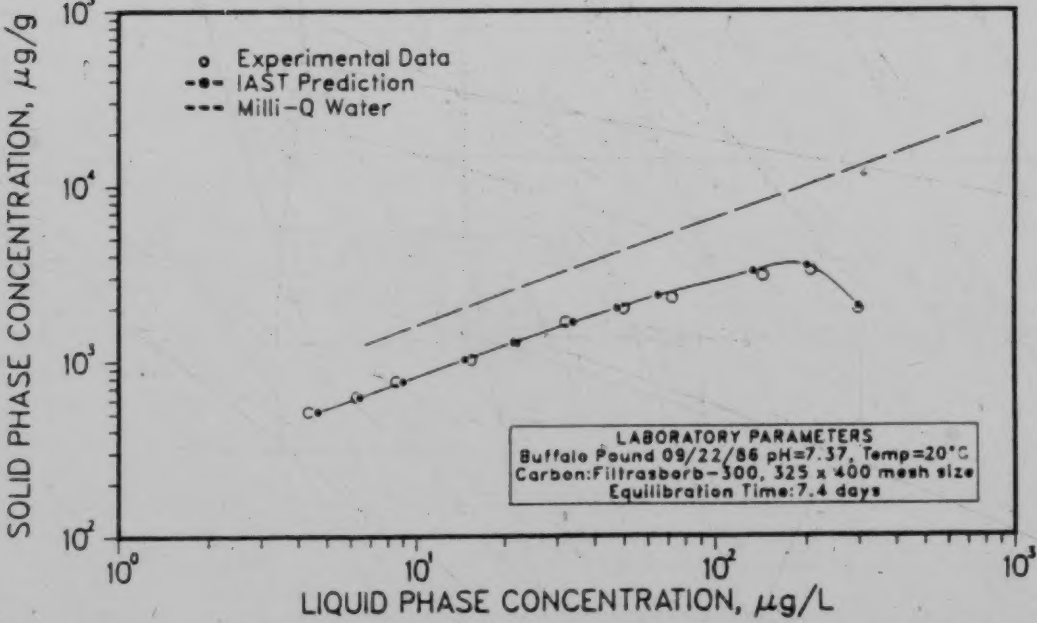


Figure V.14 IAST Prediction for Bromodichloromethane on F-300 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

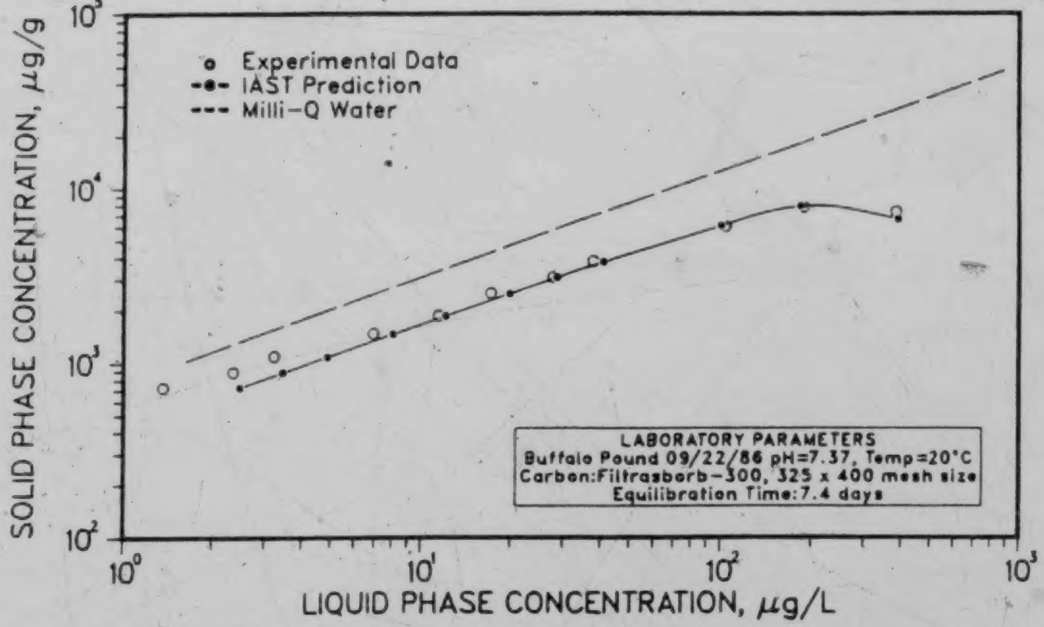


Figure V.15 IAST Prediction for Dibromochloromethane on F-300 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

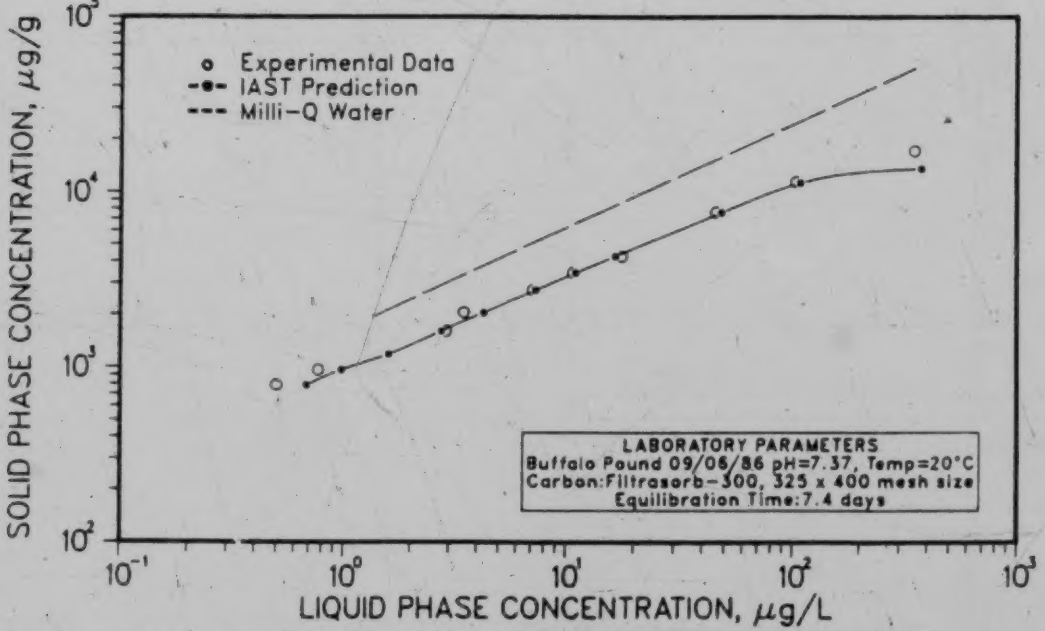


Figure V.16 IAST Prediction for Bromoform on F-300 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

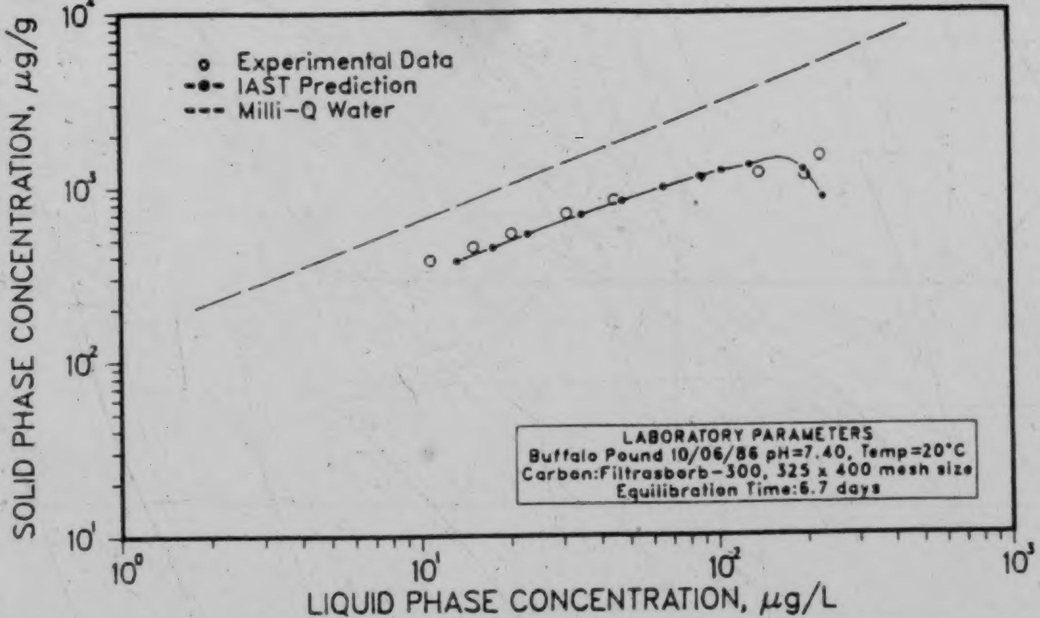


Figure V.17 IAST Prediction for Chloroform on F-300 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

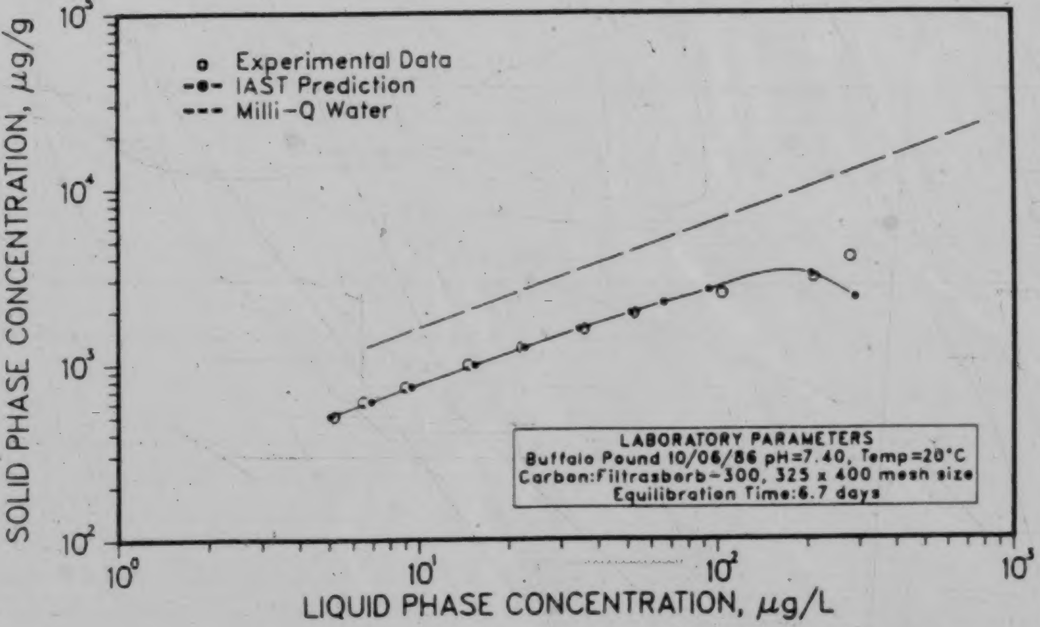


Figure V.18 IAST Prediction for Bromodichloromethane on F-300 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

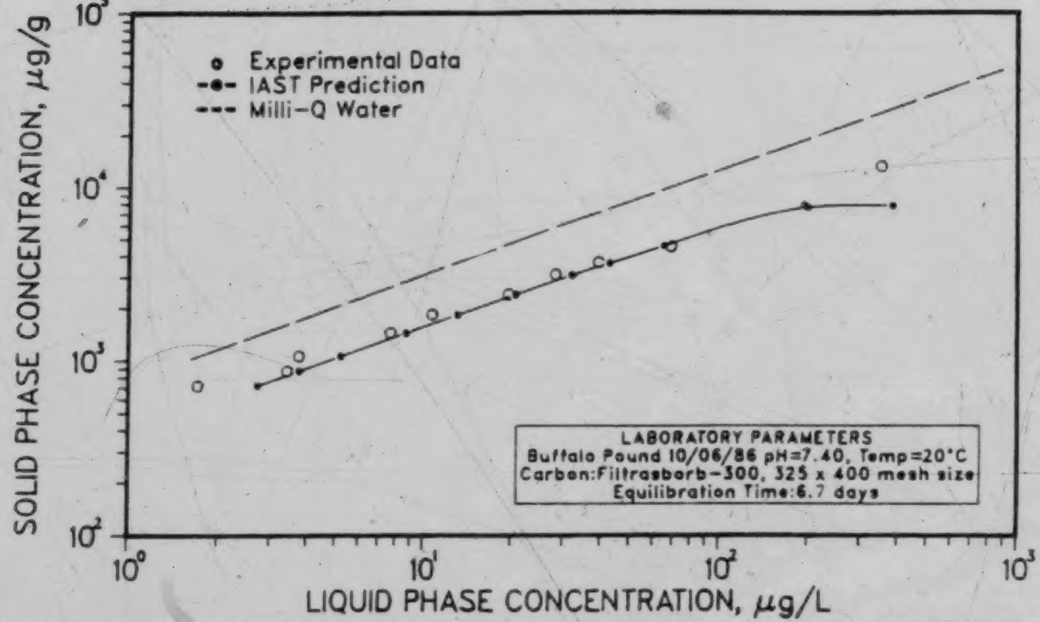


Figure V.19 IAST Prediction for Dibromochloromethane on F-300 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

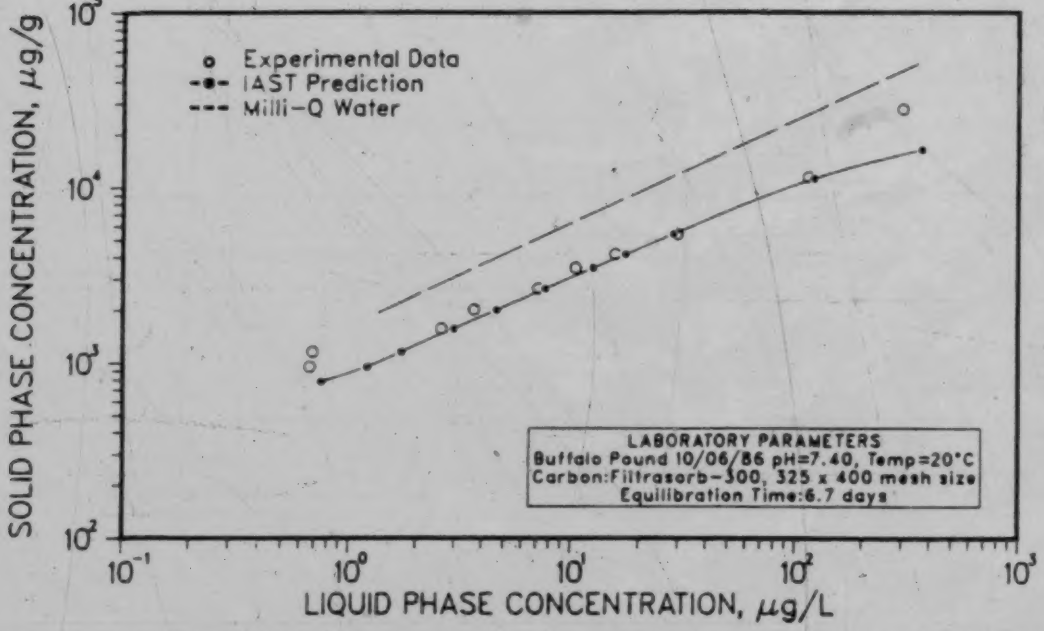


Figure V.20 IAST Prediction for Bromoform on F-300 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

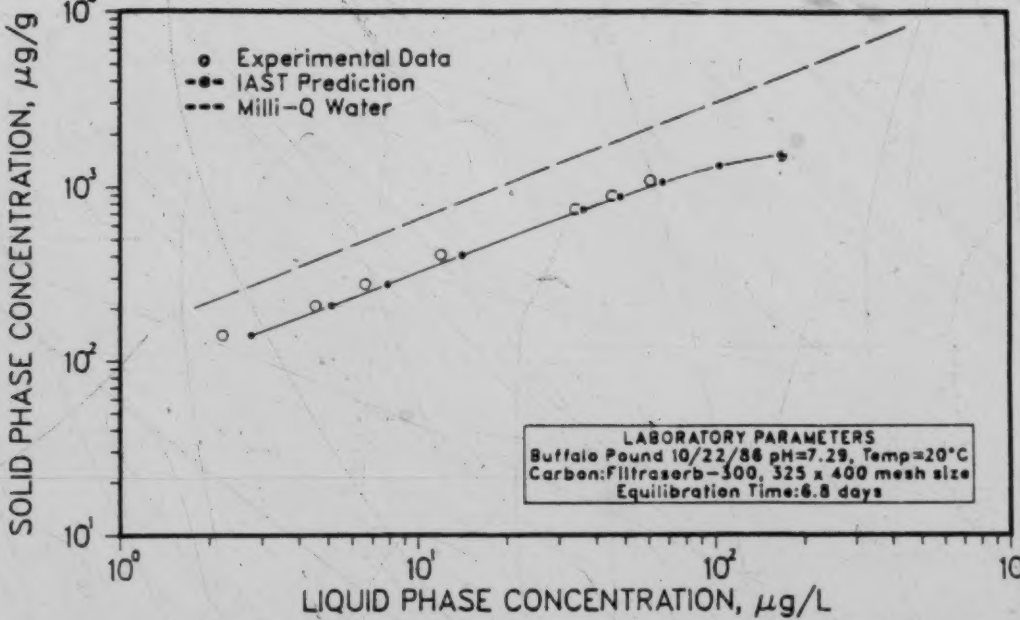


Figure V.21 IAST Prediction for Chloroform on F-300 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

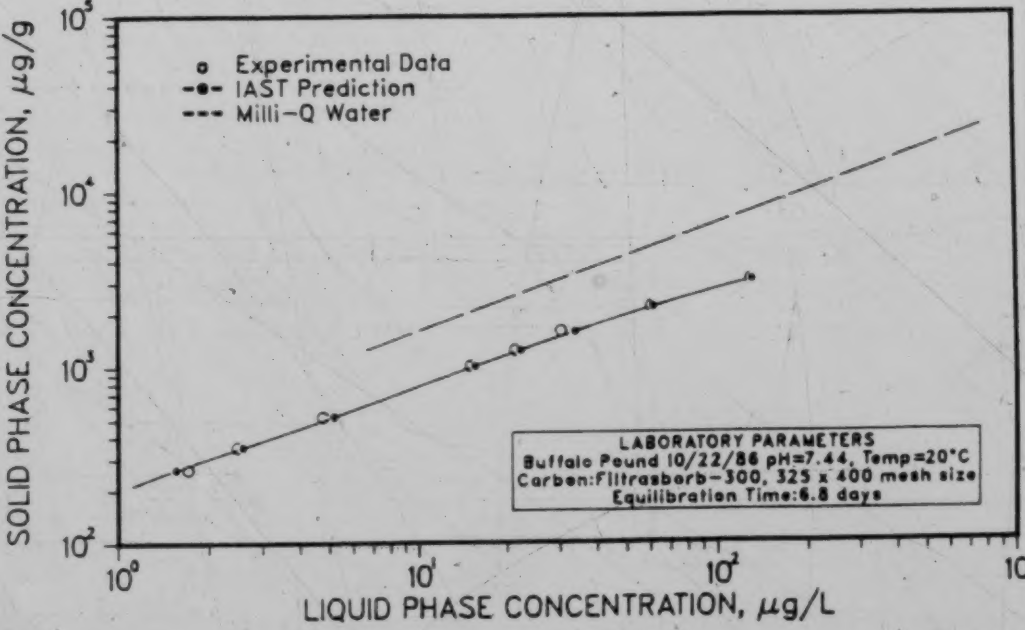


Figure V.22 IAST Prediction for Bromodichloromethane on F-300 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

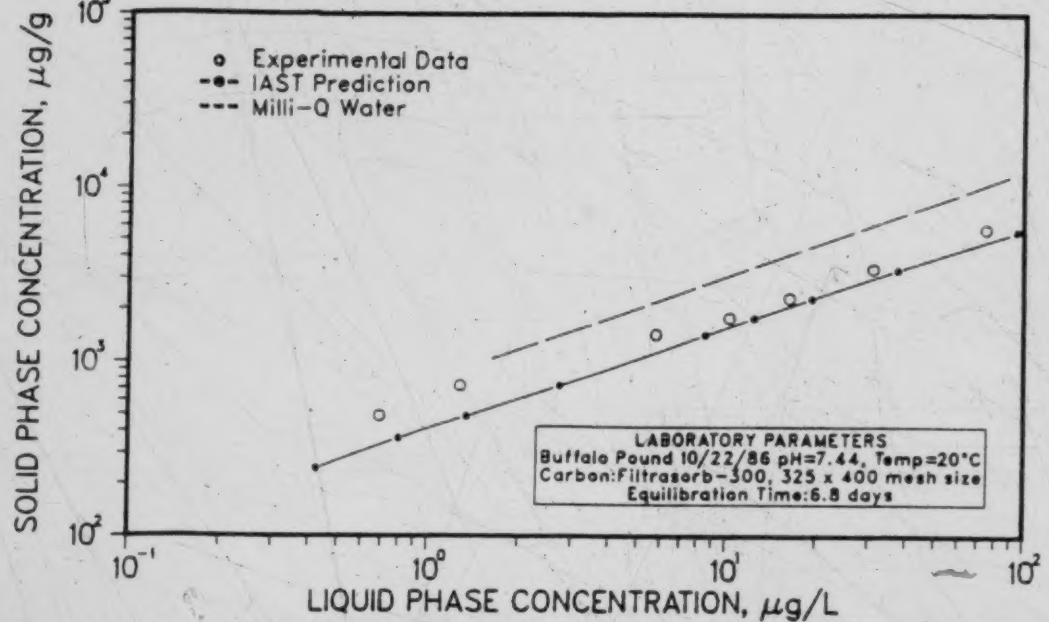


Figure V.23 IAST Prediction for Dibromochloromethane on F-300 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

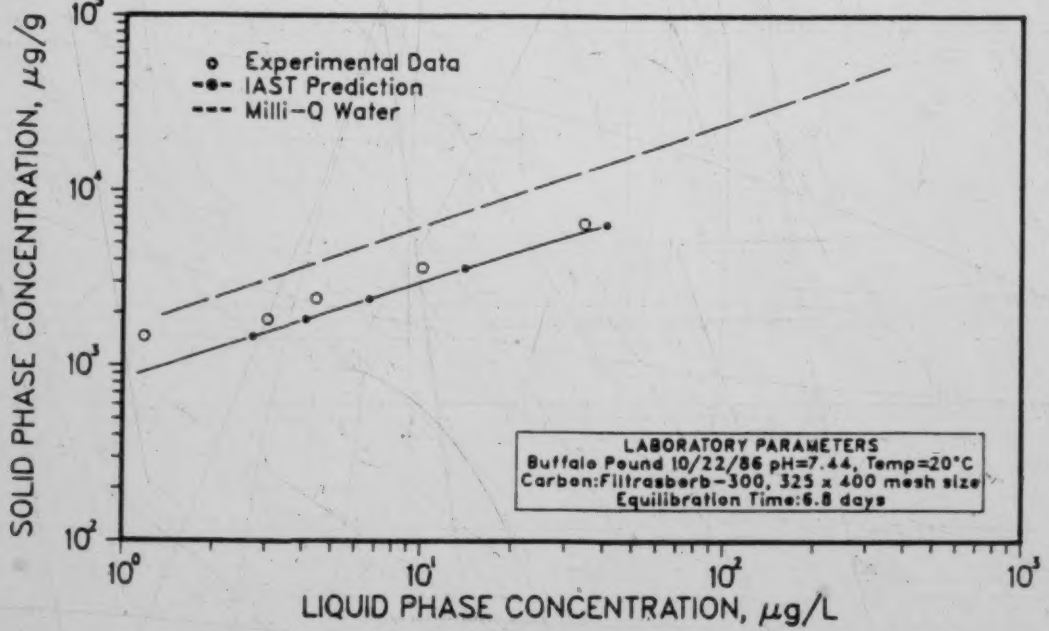


Figure V.24 IAST Prediction for Bromoform on F-300 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

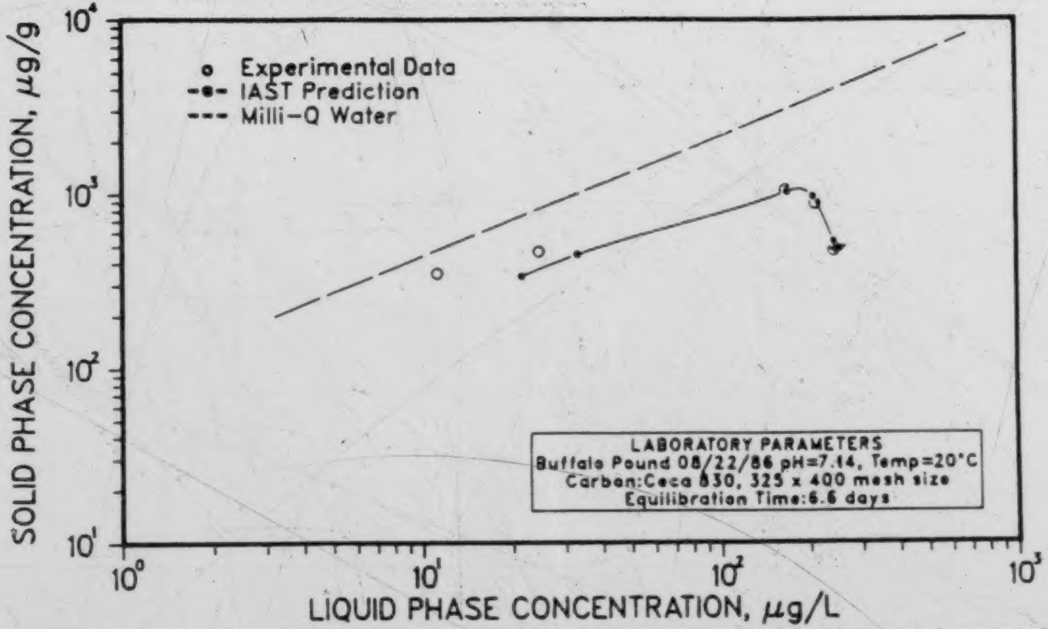


Figure V.25 IAST Prediction for Chloroform on Ceca 830 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

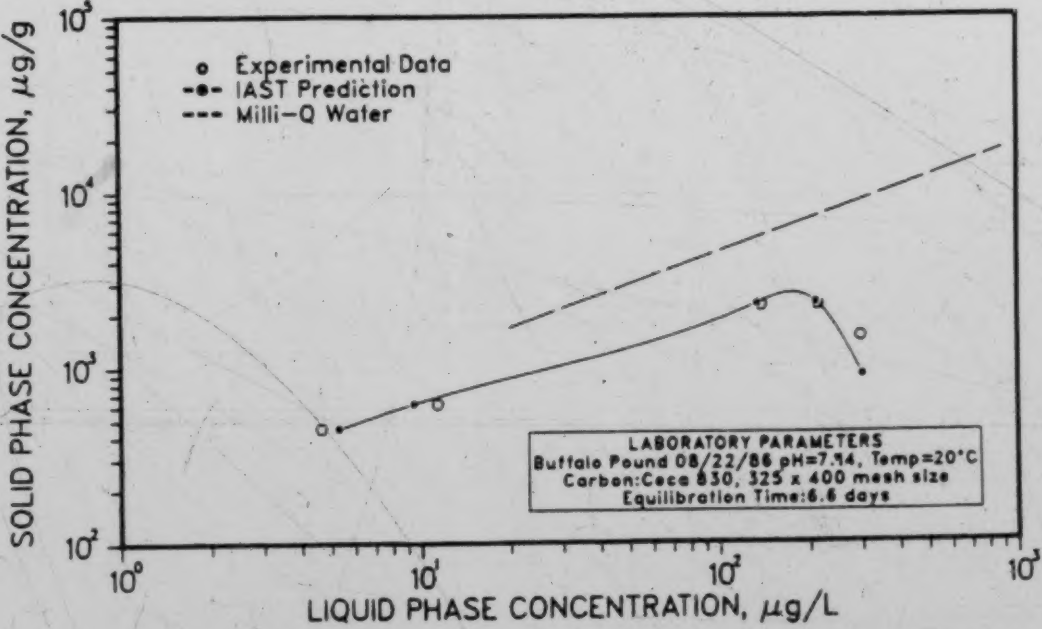


Figure V.26 IAST Prediction for Bromodichloromethane on Ceca 830 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

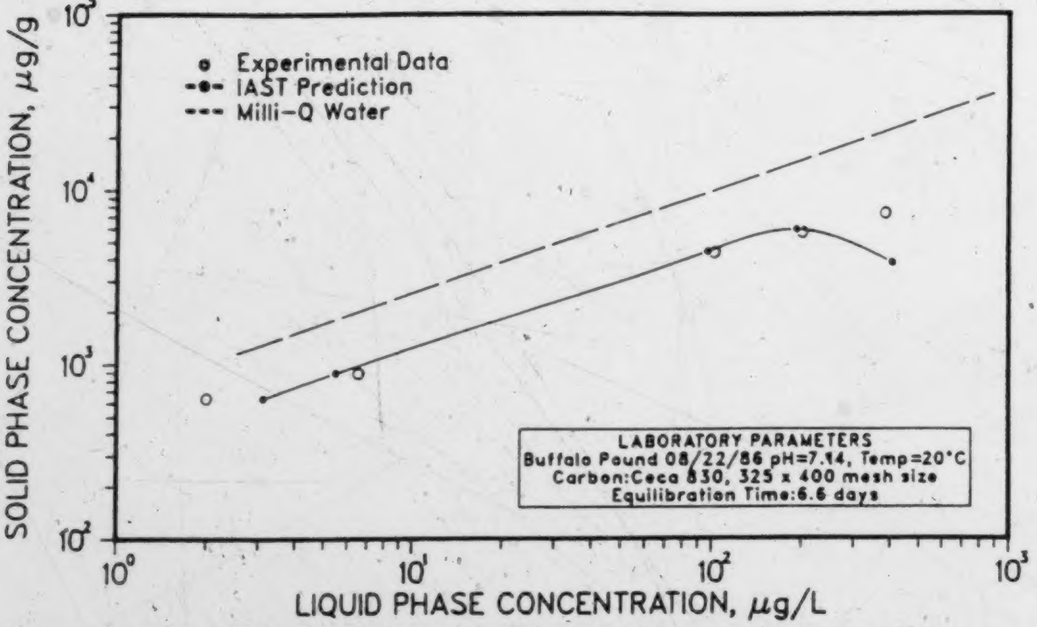


Figure V.27 IAST Prediction for Dibromochloromethane on Ceca 830 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

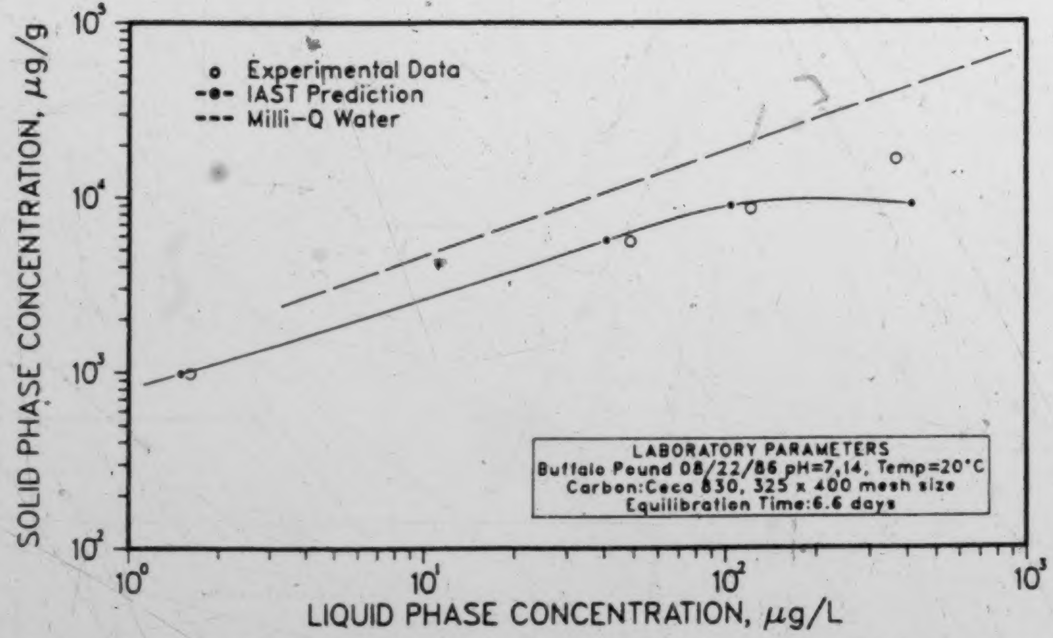


Figure V.28 IAST Prediction for Bromoform on Ceca 830 in August 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

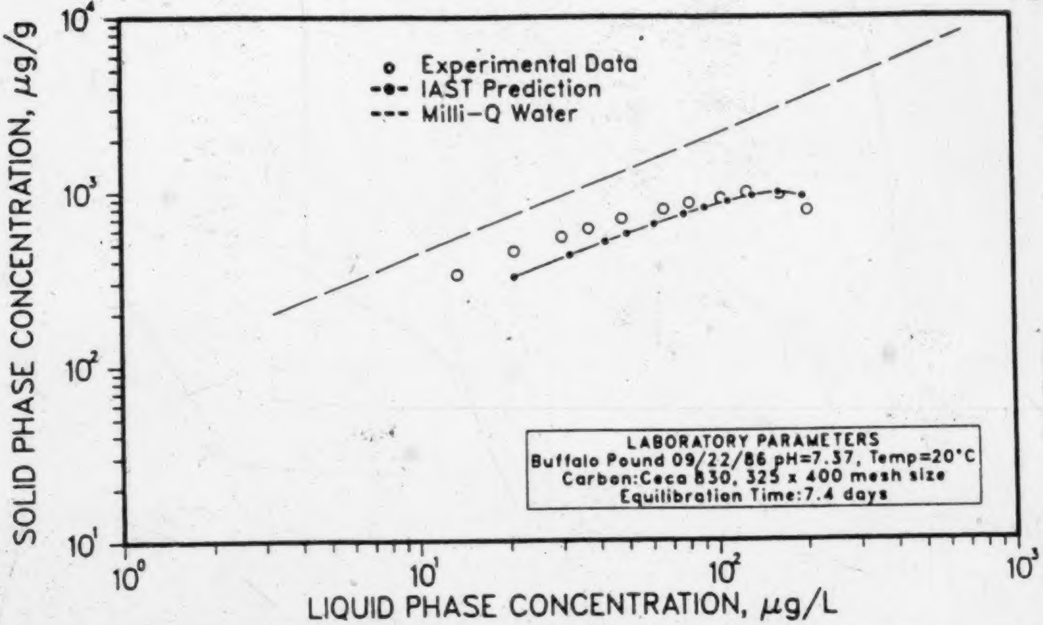


Figure V.29 IAST Prediction for Chloroform on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

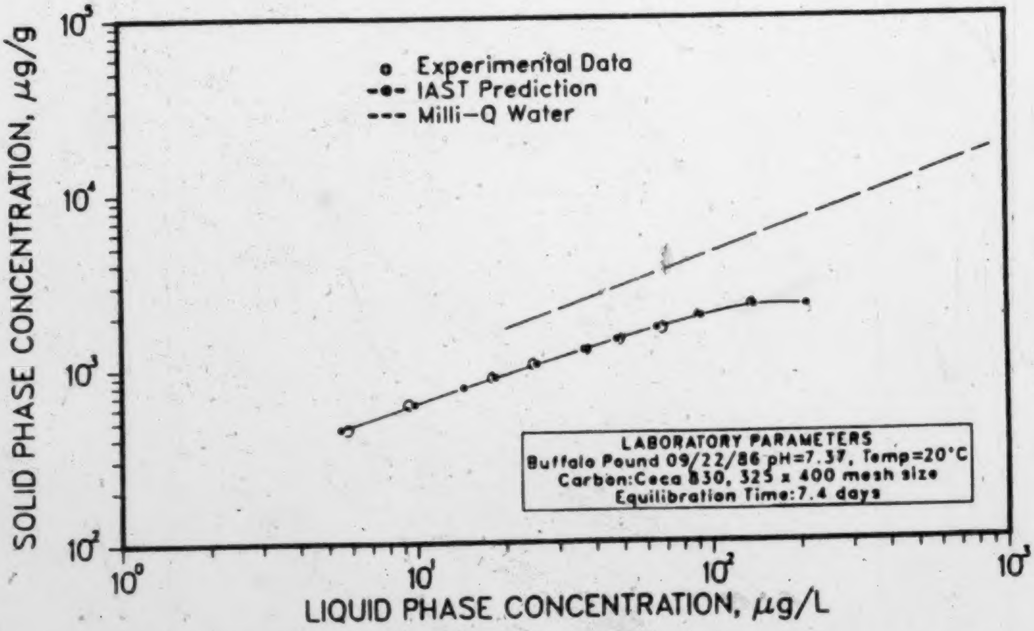


Figure V.30 IAST Prediction for Bromodichloromethane on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

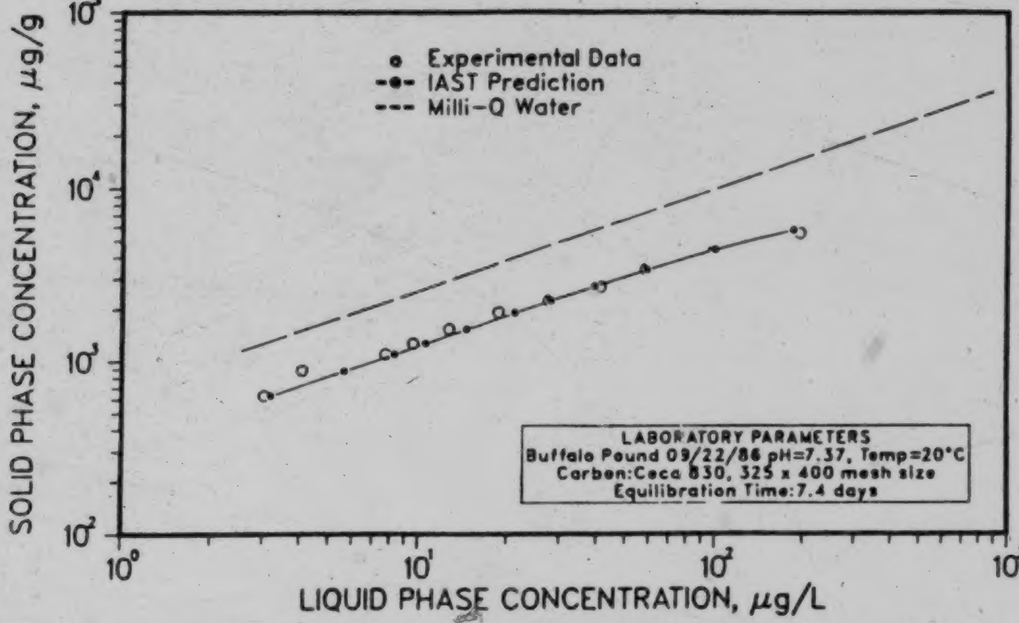


Figure V.31 IAST Prediction for Dibromochloromethane on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

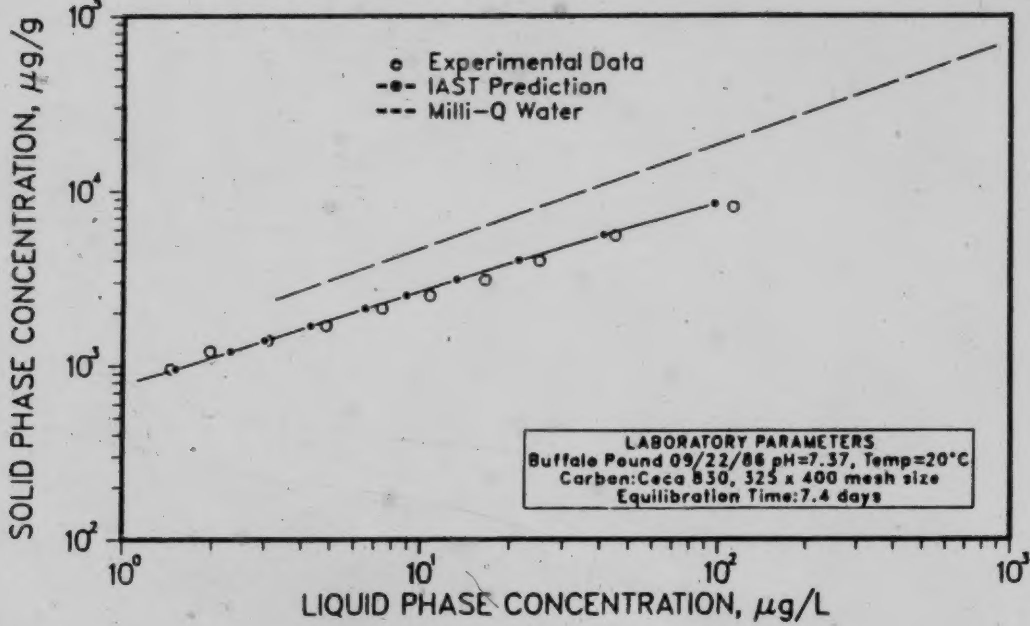


Figure V.32 IAST Prediction for Bromoform on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

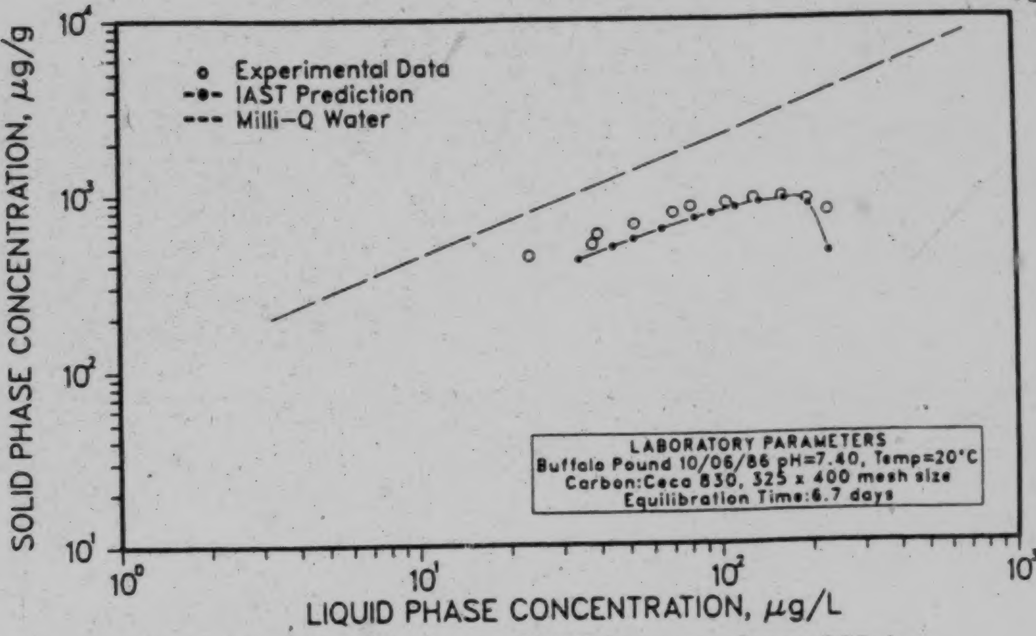


Figure V.33 IAST Prediction for Chloroform on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

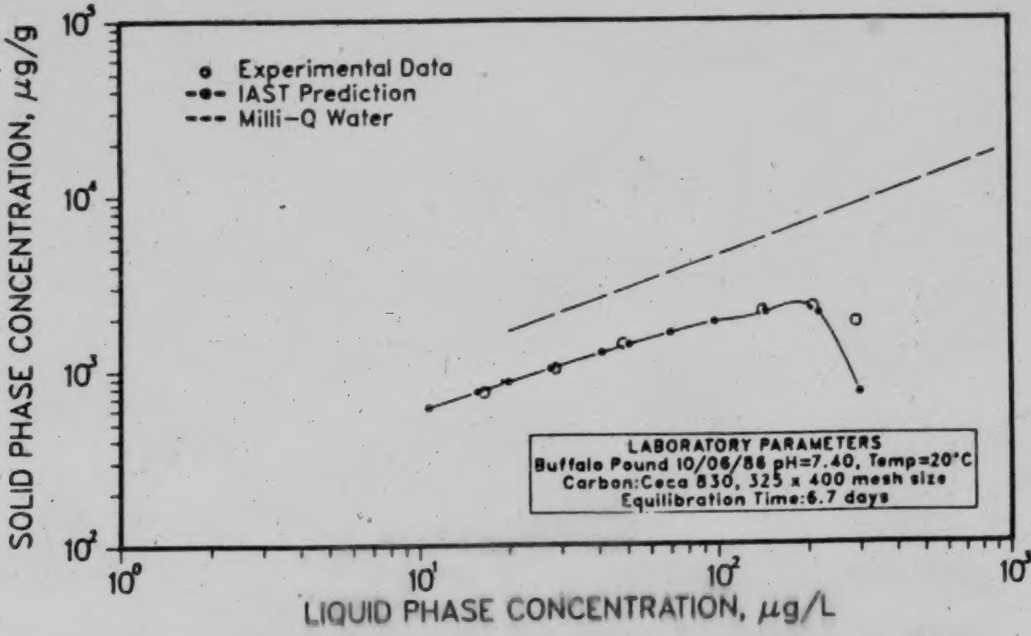


Figure V.34 IAST Prediction for Bromodichloromethane on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

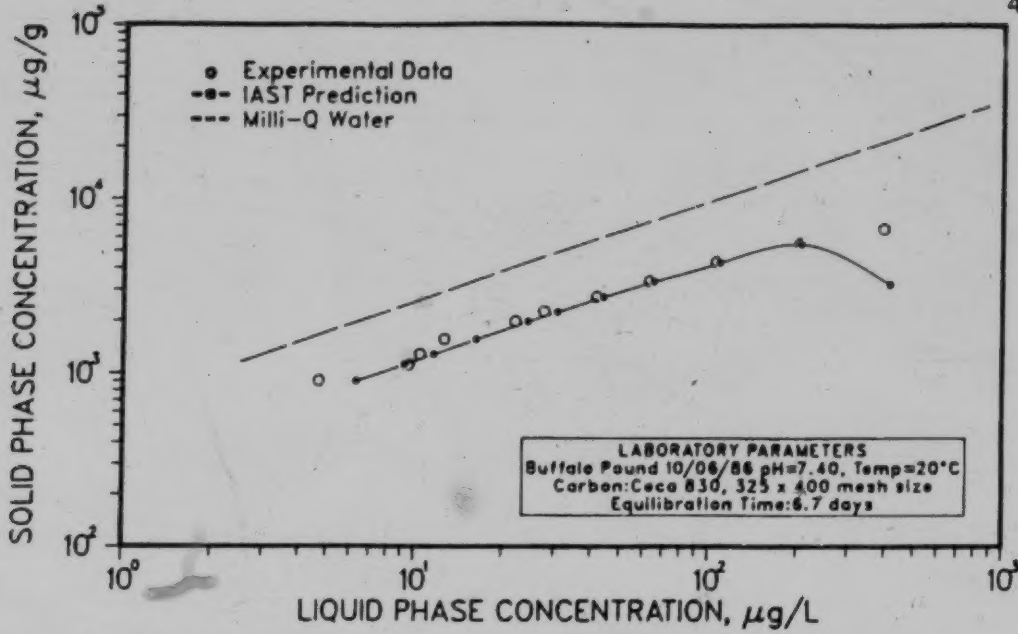


Figure V.35 IAST Prediction for Dibromochloromethane on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

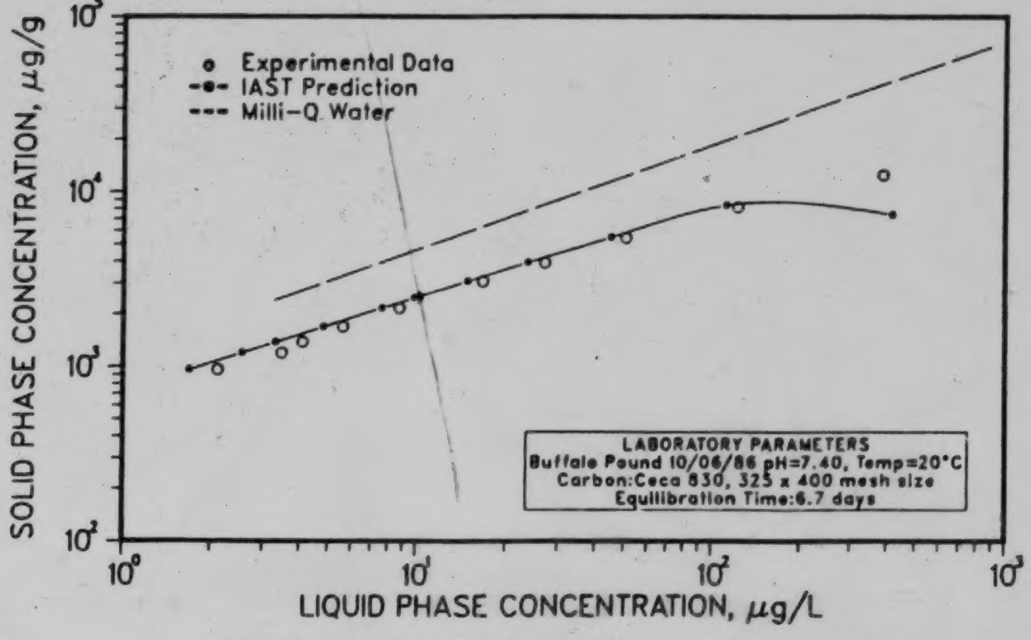


Figure V.36 IAST Prediction for Bromoform on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

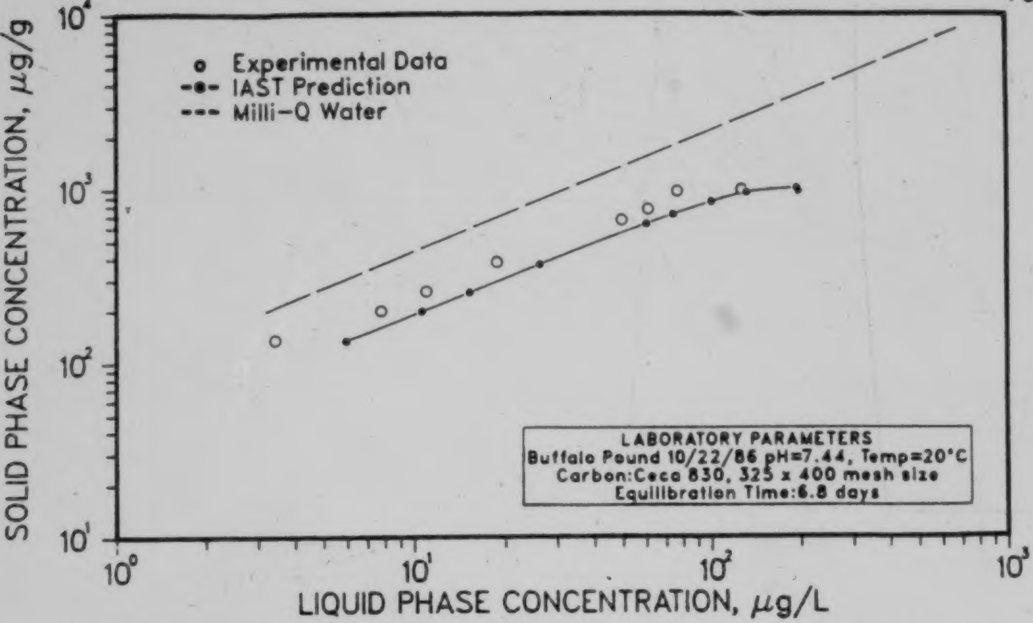


Figure V.37 IAST Prediction for Chloroform on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

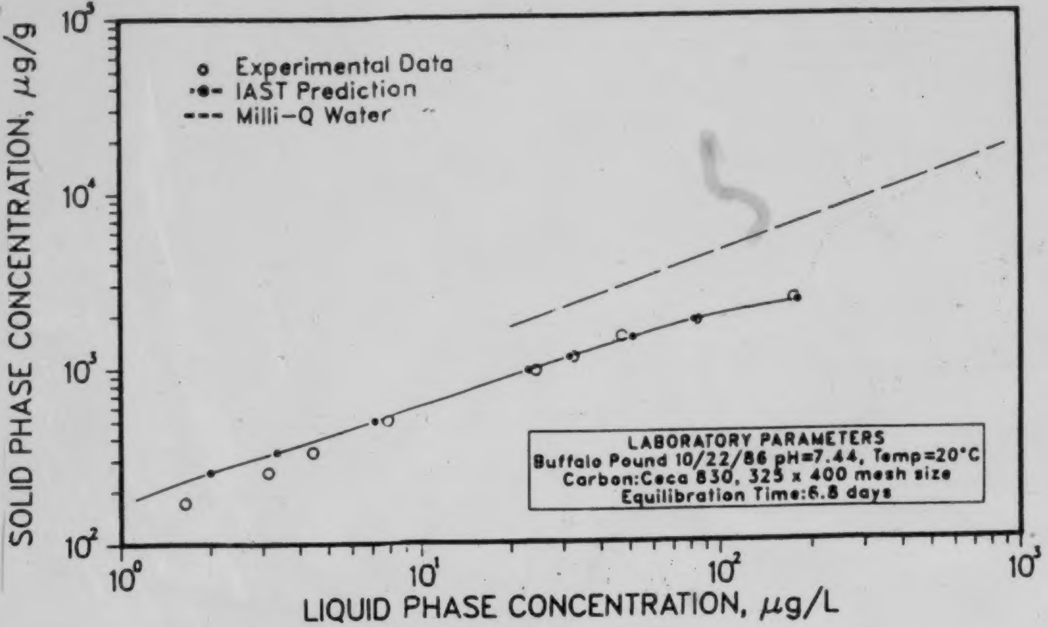


Figure V.38 IAST Prediction for Bromodichloromethane on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

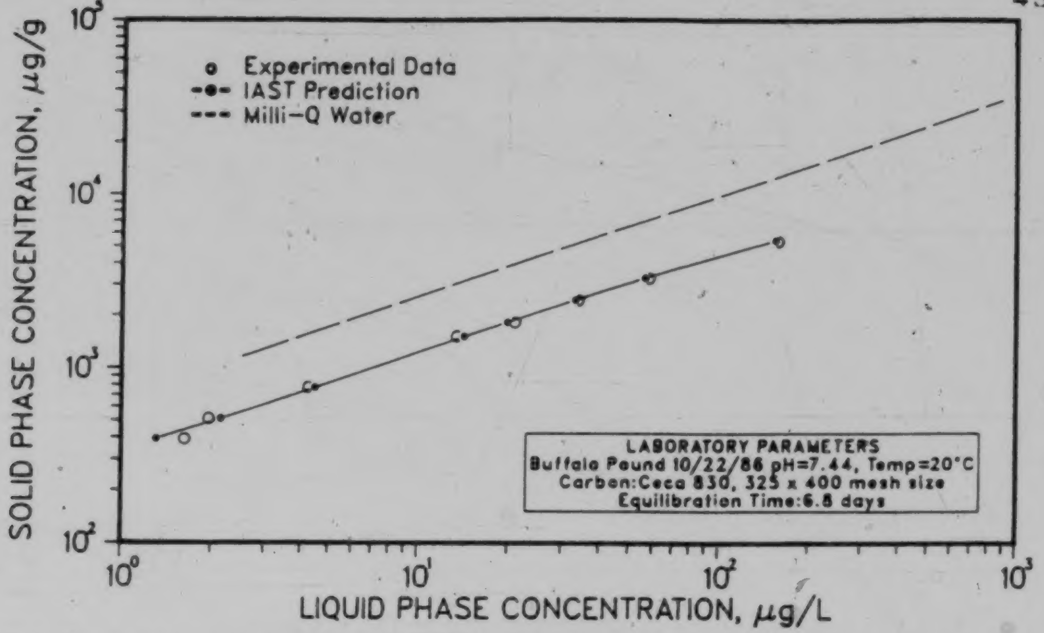


Figure V.39 IAST Prediction for Dibromochloromethane on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

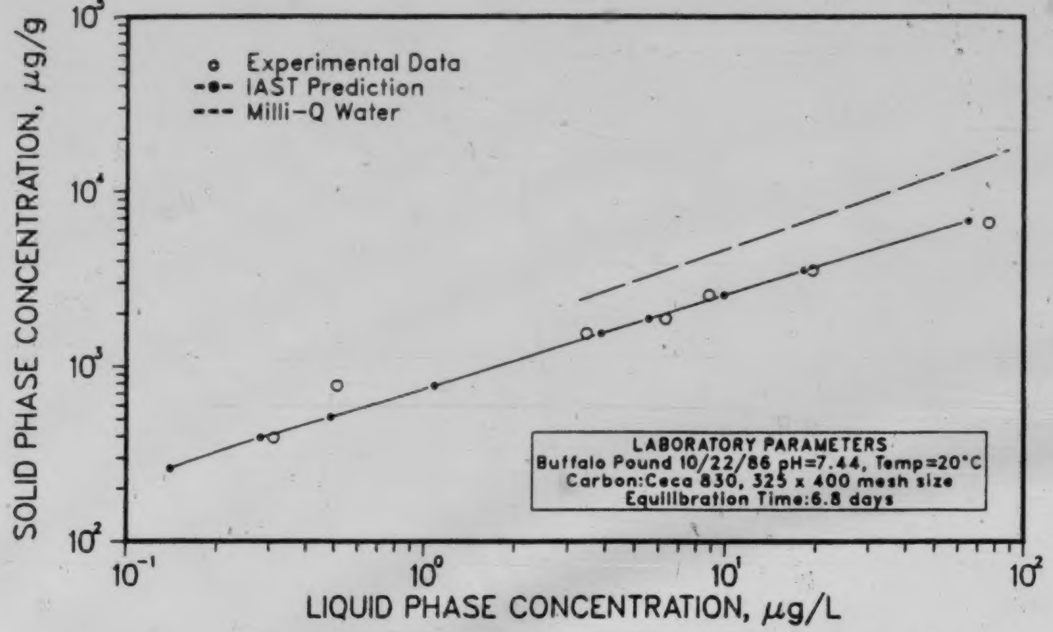


Figure V.40 IAST Prediction for Bromoform on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using HC's Fit to Bromodichloromethane

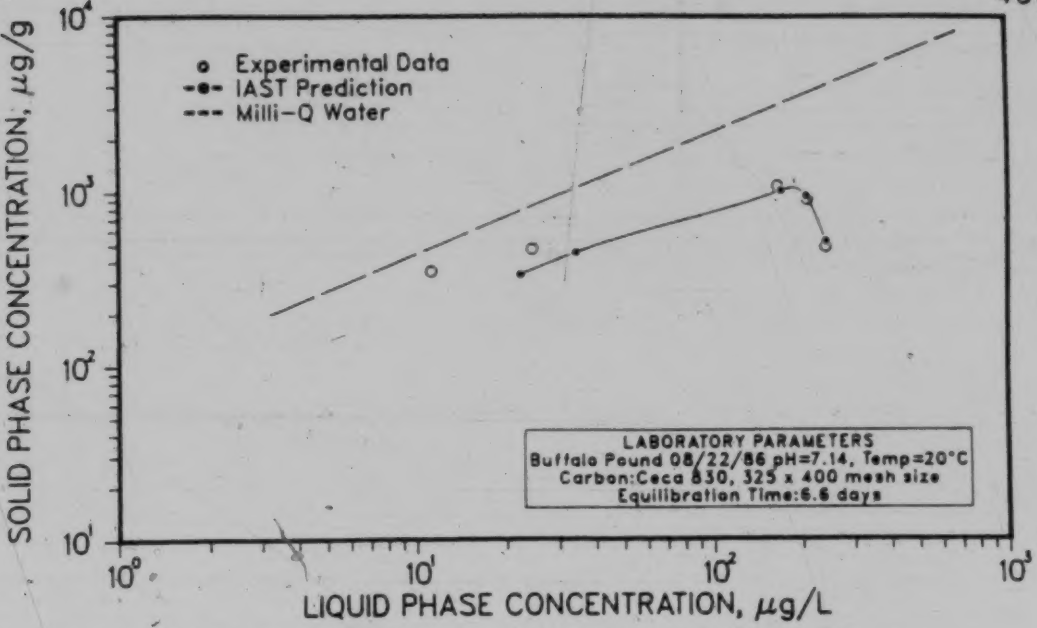


Figure V.41 IAST Prediction for Chloroform on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

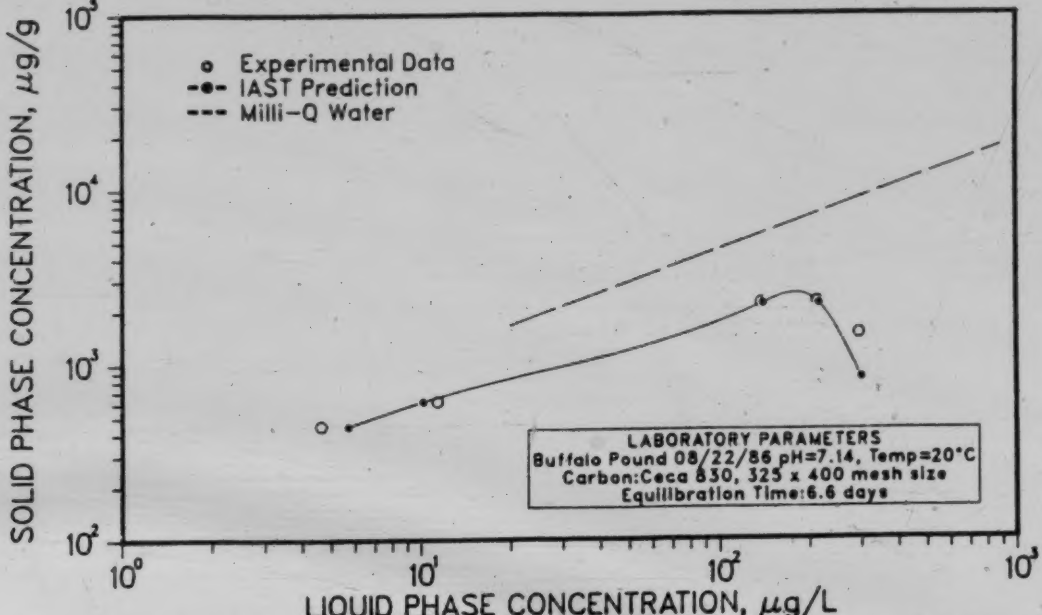


Figure V.42 IAST Prediction for Bromodichloromethane on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

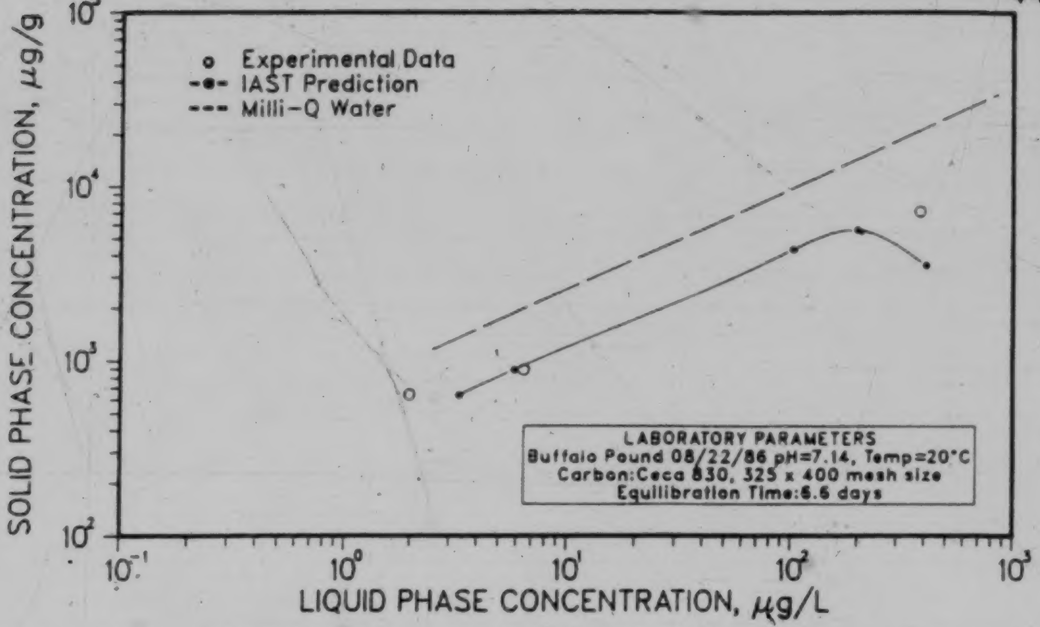


Figure V.43 IAST Prediction for Dibromochloromethane on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

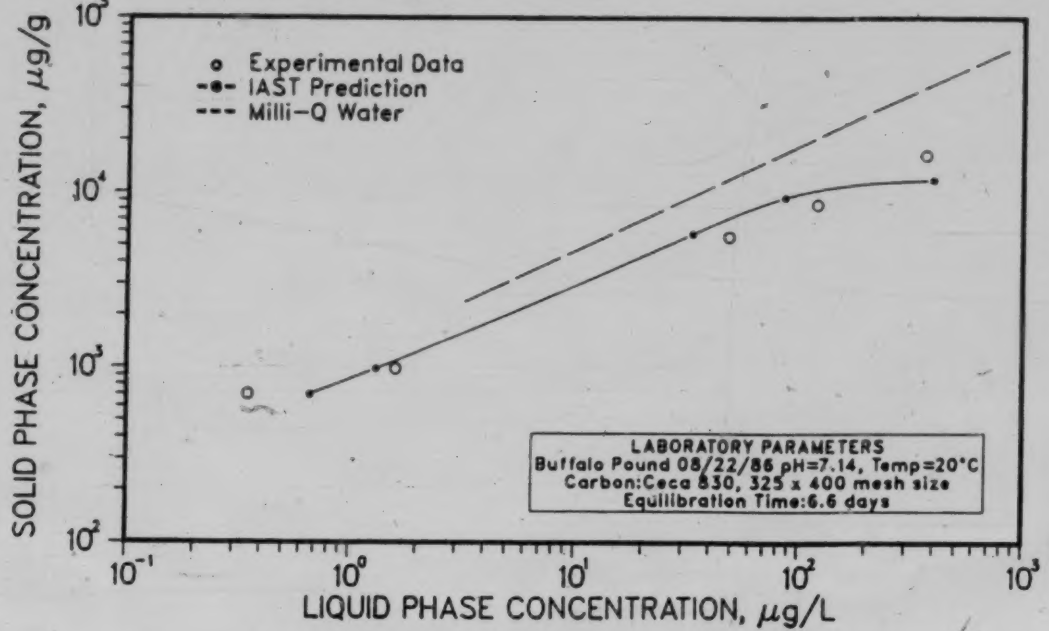


Figure V.44 IAST Prediction for Bromoform on Ceca 830 in September 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

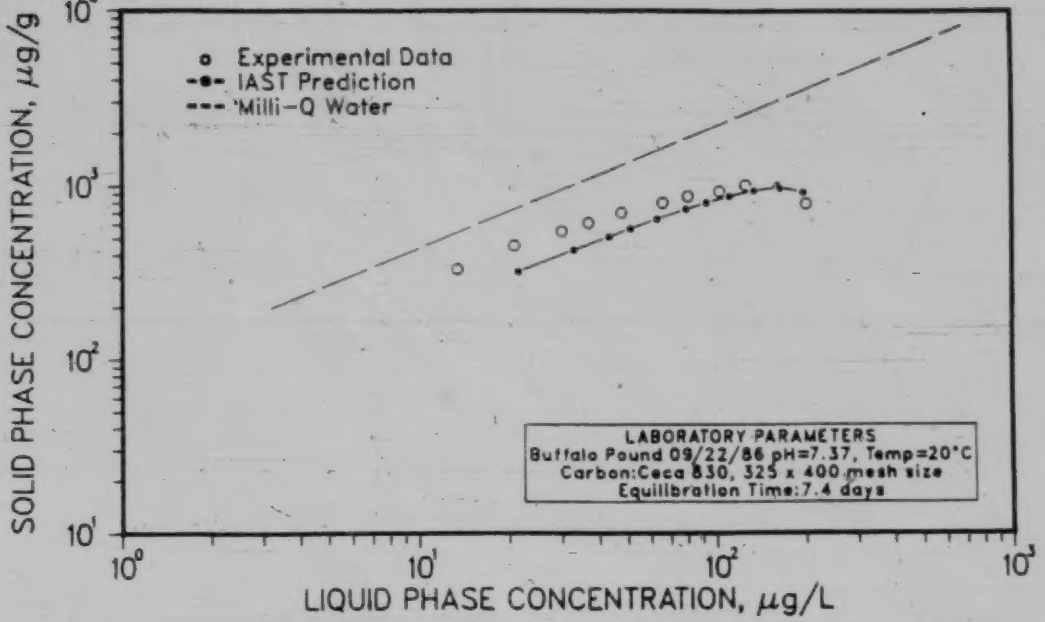


Figure V.45 IAST Prediction for Chloroform on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

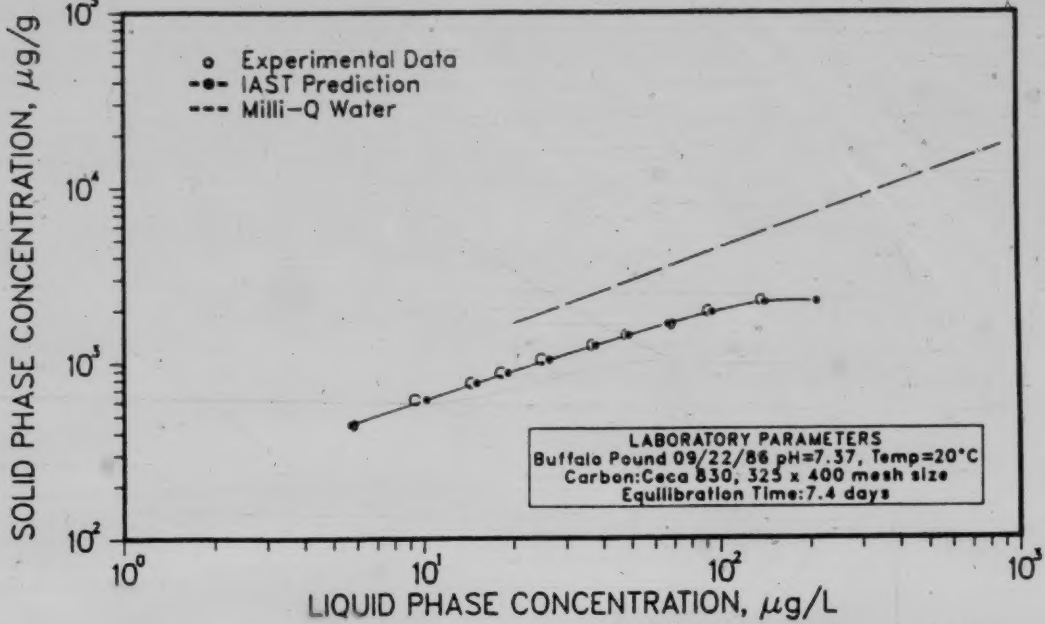


Figure V.46 IAST Prediction for Bromodichloromethane on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

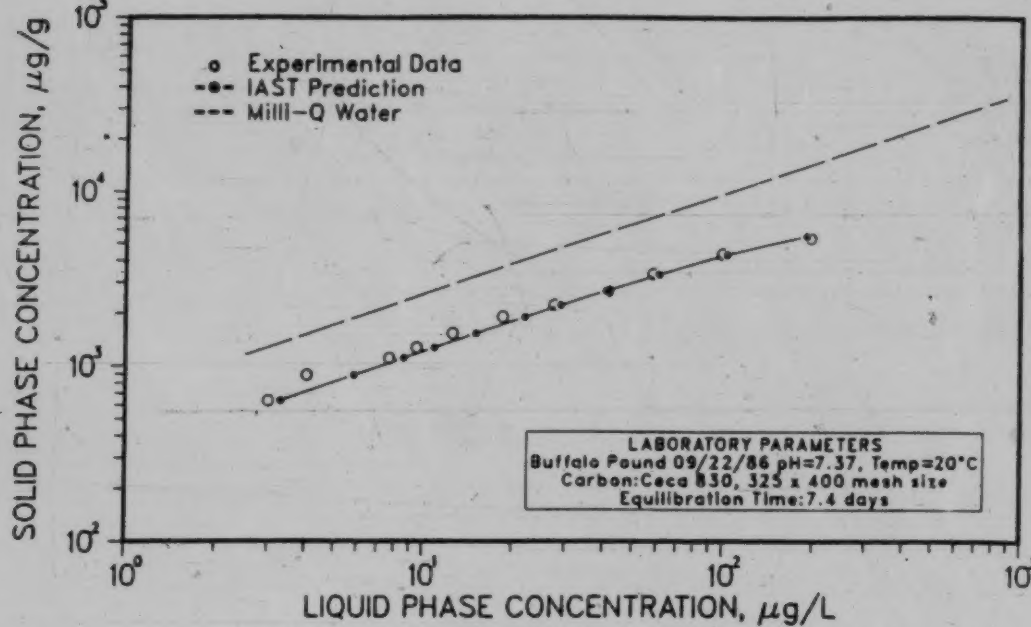


Figure V.47 IAST Prediction for Dibromochloromethane on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

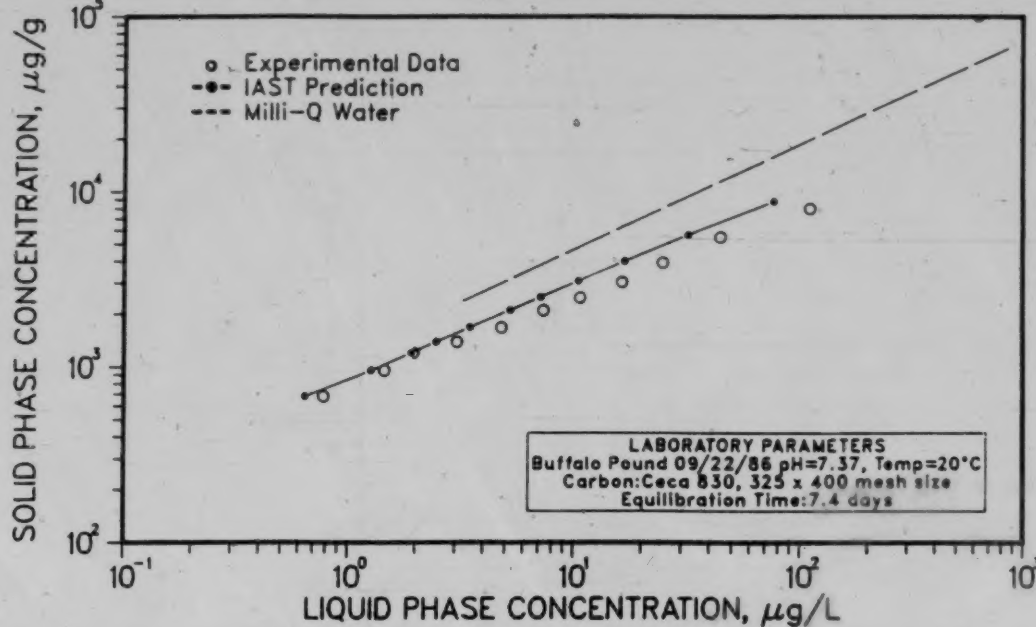


Figure V.48 IAST Prediction for Bromoform on Ceca 830 in October 6, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

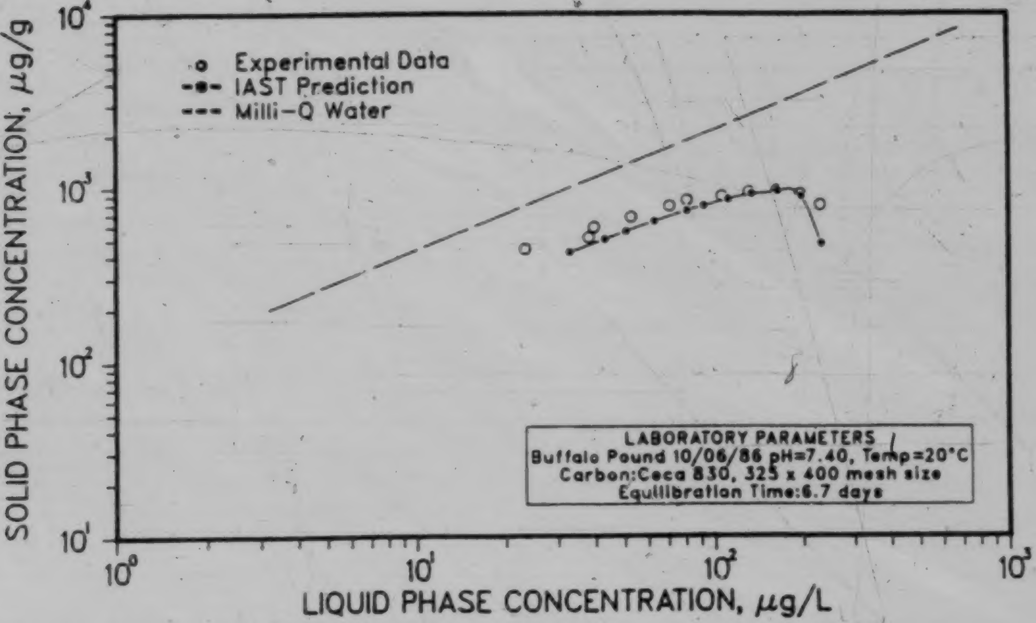


Figure V.49 IAST Prediction for Chloroform on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

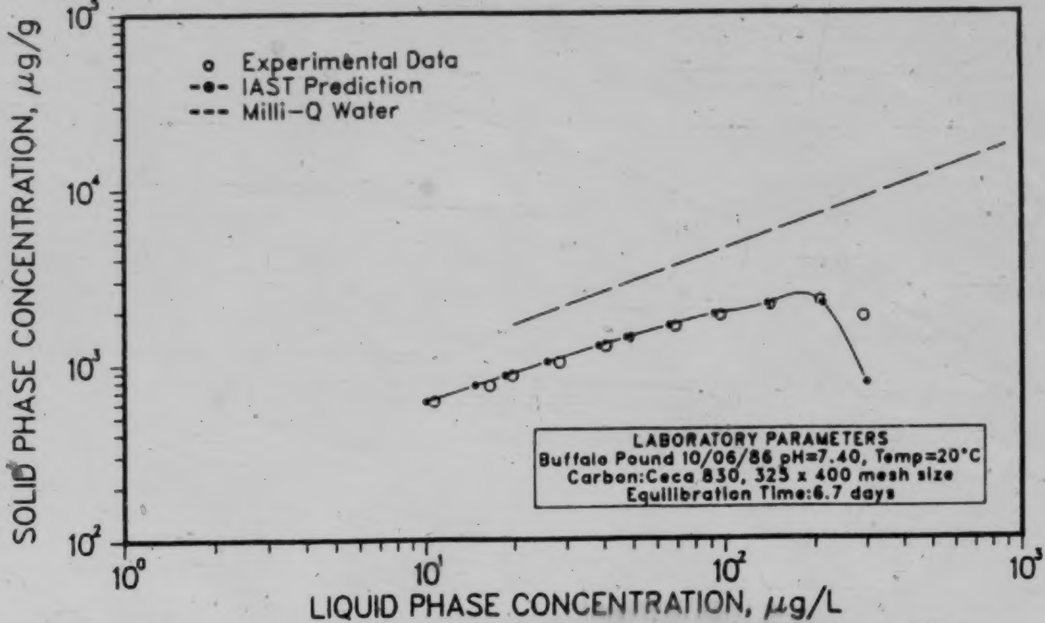


Figure V.50 IAST Prediction for Bromodichloromethane on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

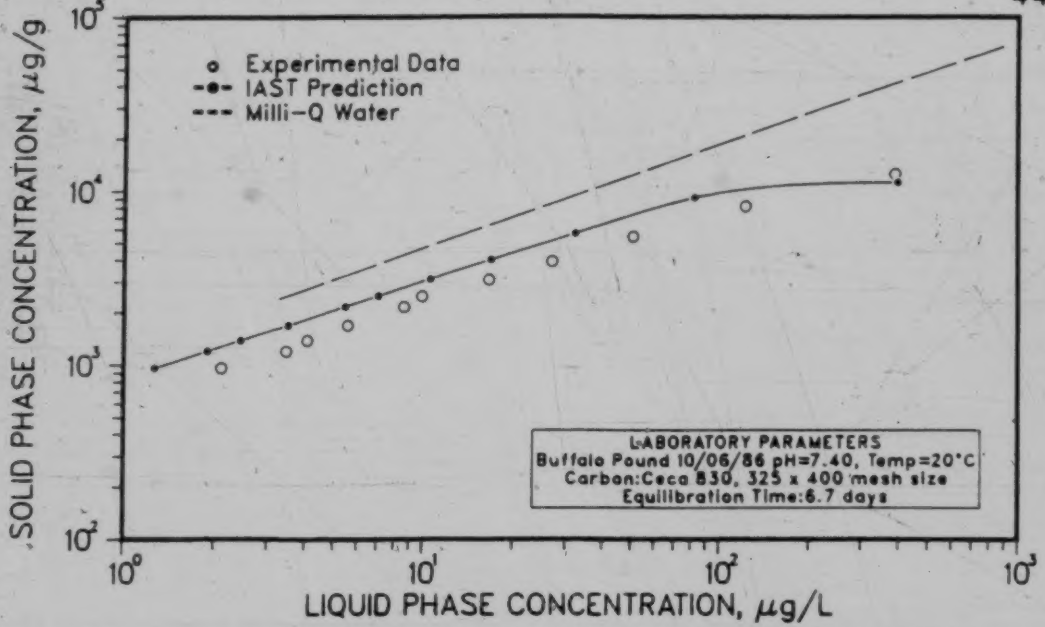


Figure V.51 IAST Prediction for Dibromochloromethane on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

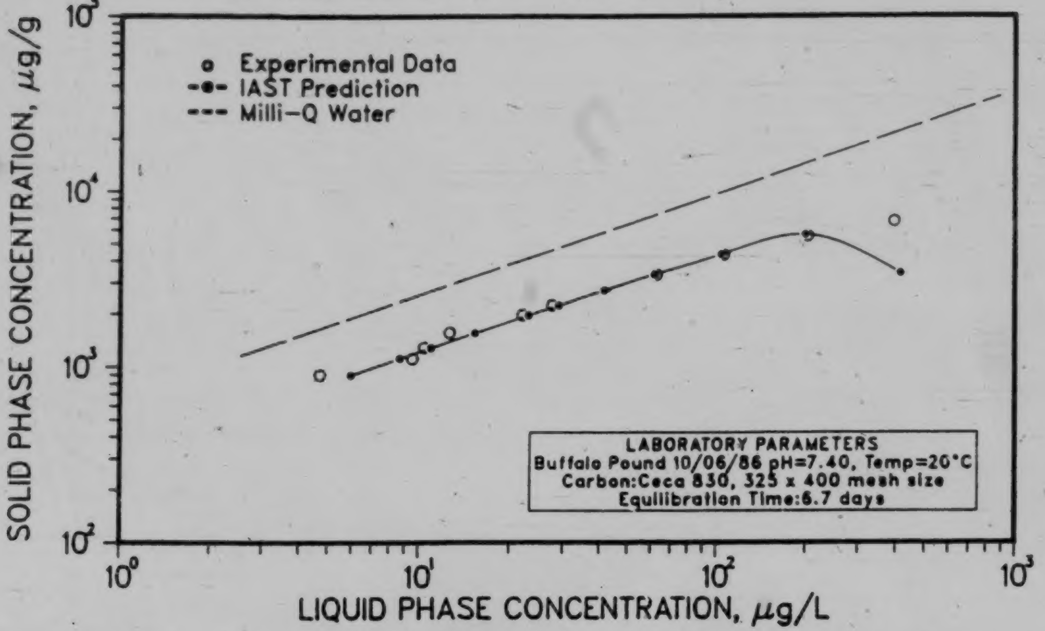


Figure V.52 IAST Prediction for Bromoform on Ceca 830 in October 22, 1986 Buffalo Pound Water Matrix Using Means of HC's Fit to Bromodichloromethane

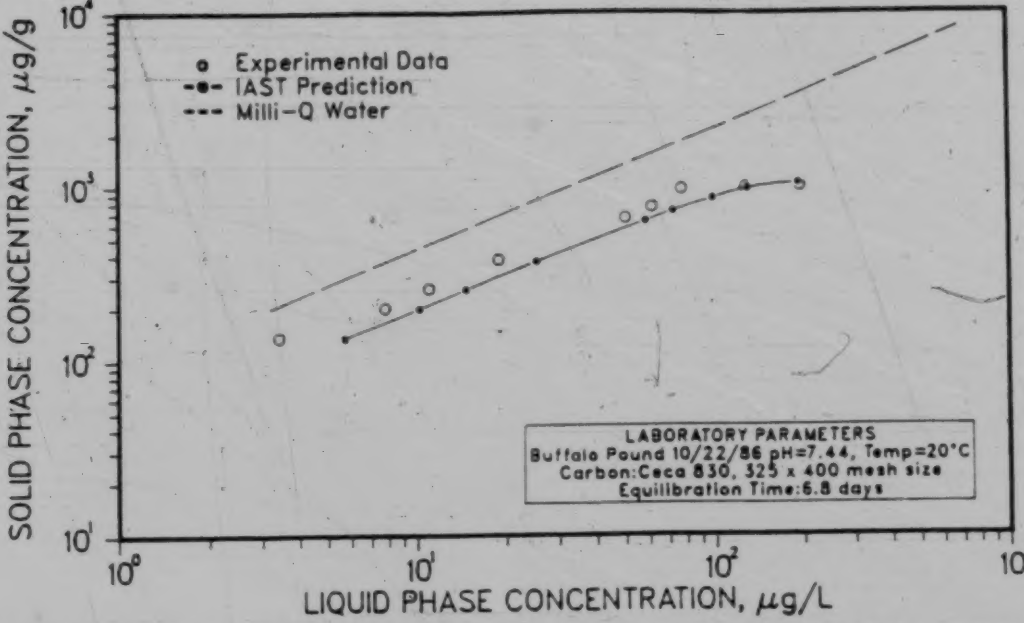


Figure V.53 Effect of Varying K by 10% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

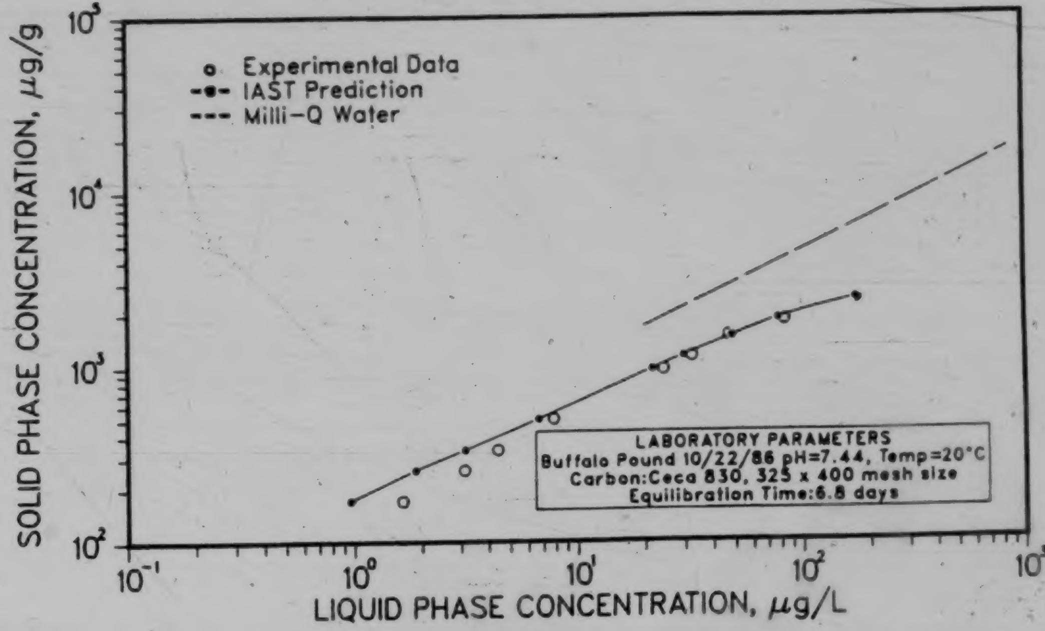


Figure V.54 Effect of Varying K by 50% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

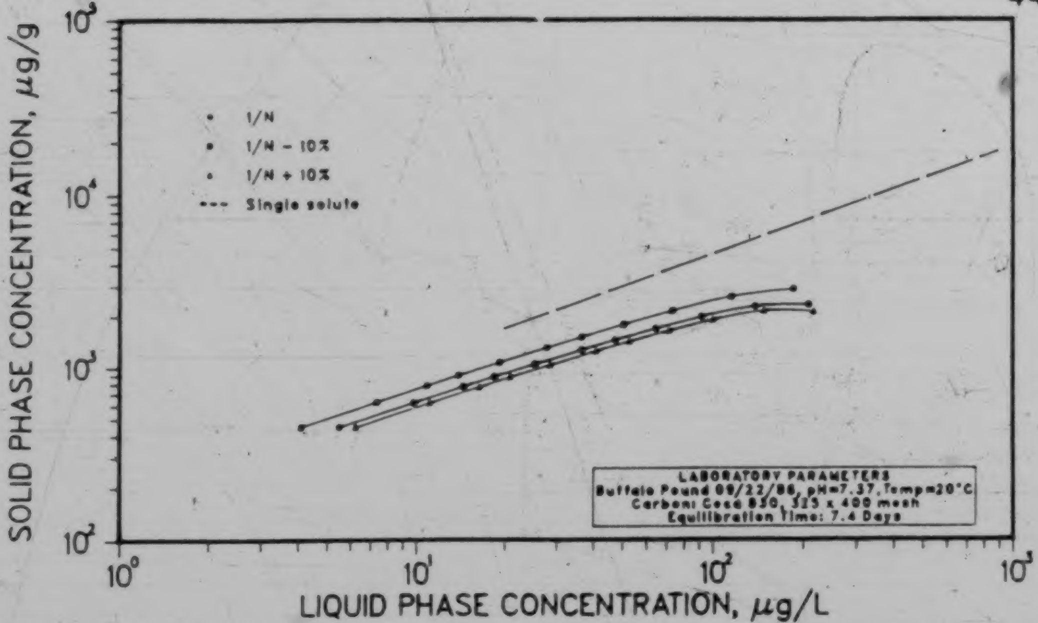


Figure V.55 Effect of Varying 1/n by 10% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

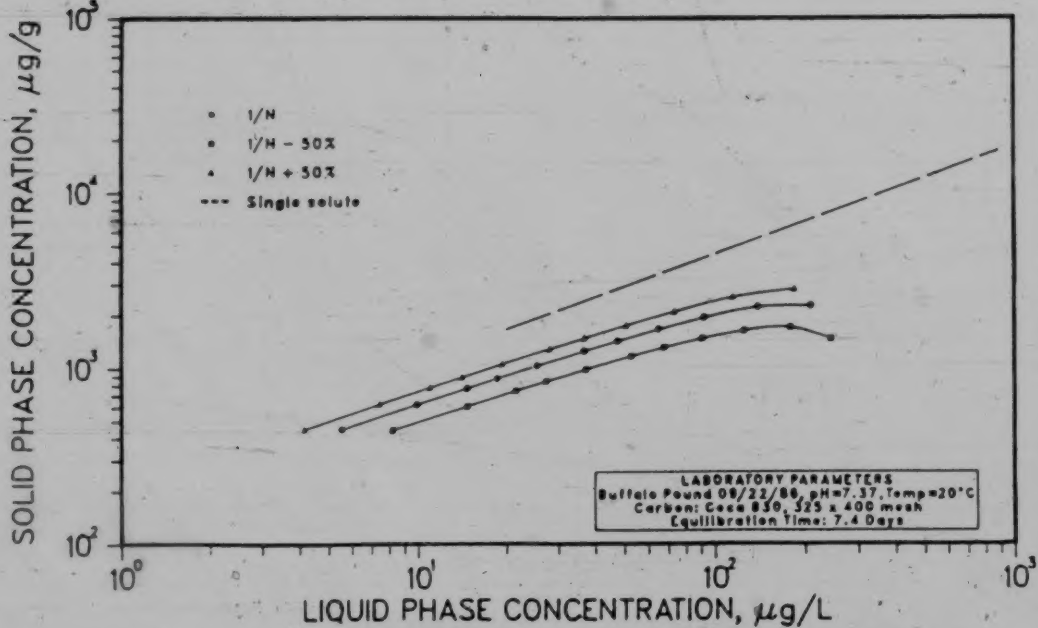


Figure V.56 Effect of Varying 1/n by 50% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

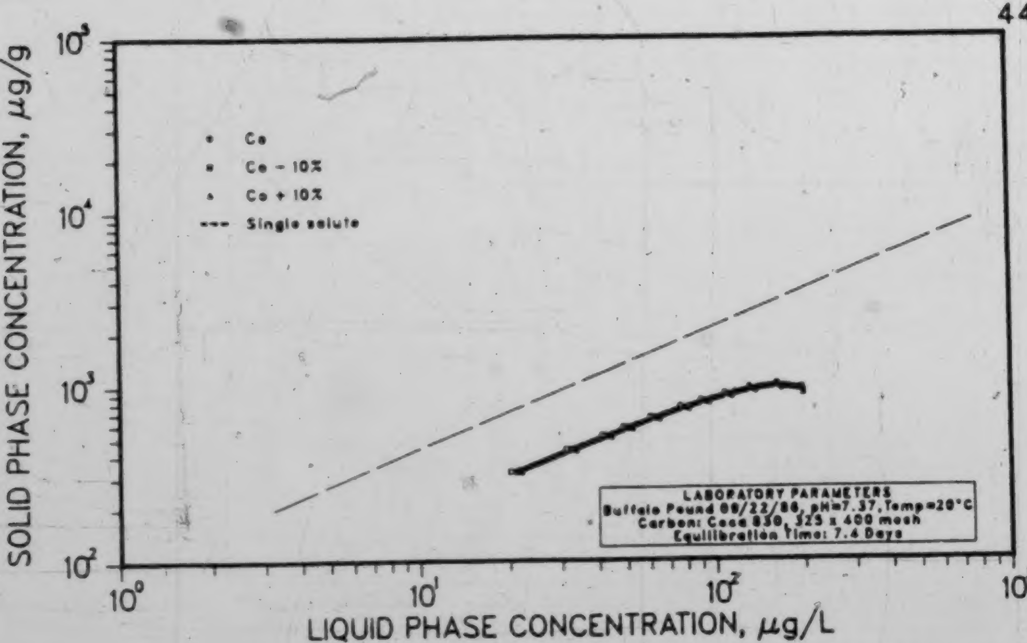


Figure V.57 Effect of Varying C_0 by 10% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

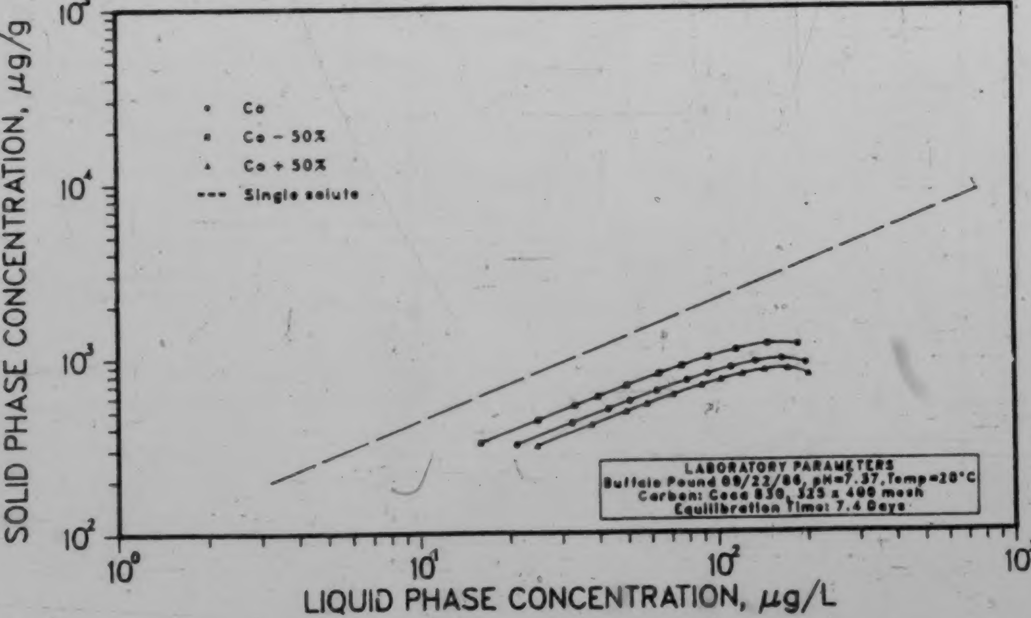


Figure V.58 Effect of Varying C_0 by 50% Upon IAST Predictions for Bromodichloromethane Using HC's Fit to Bromodichloromethane

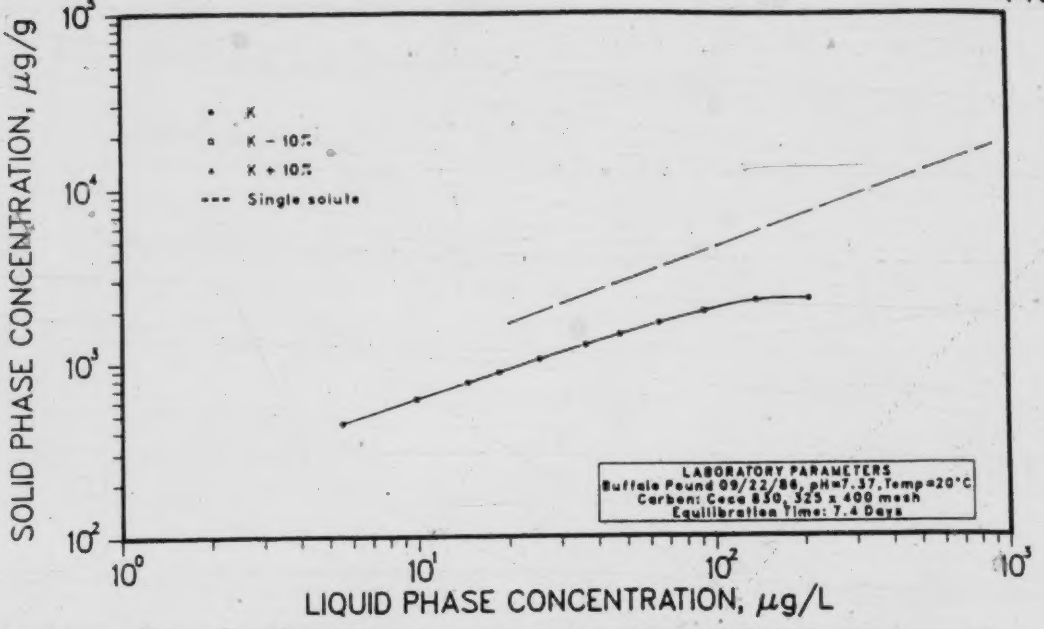


Figure V.59 Effect of Varying K by 10% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

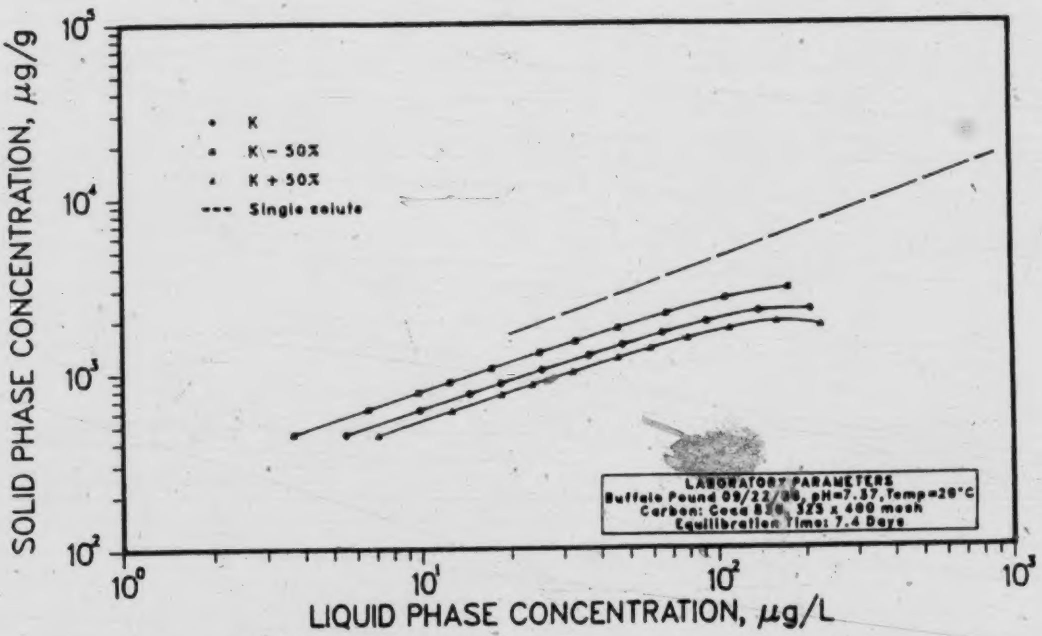


Figure V.60 Effect of Varying K by 50% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

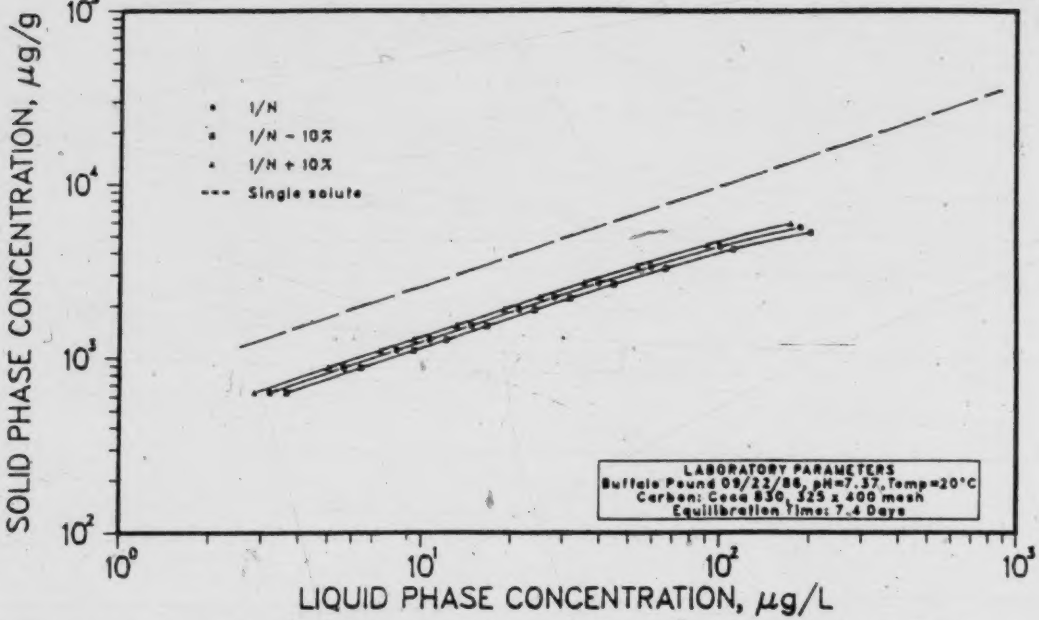


Figure V.61 Effect of Varying 1/n by 10% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

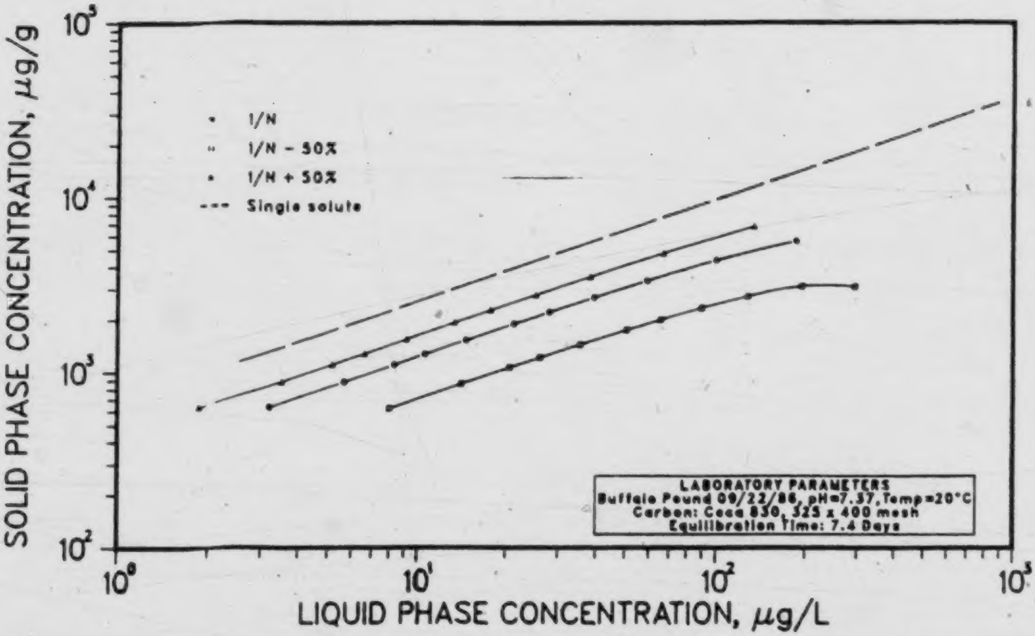


Figure V.62 Effect of Varying 1/n by 50% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

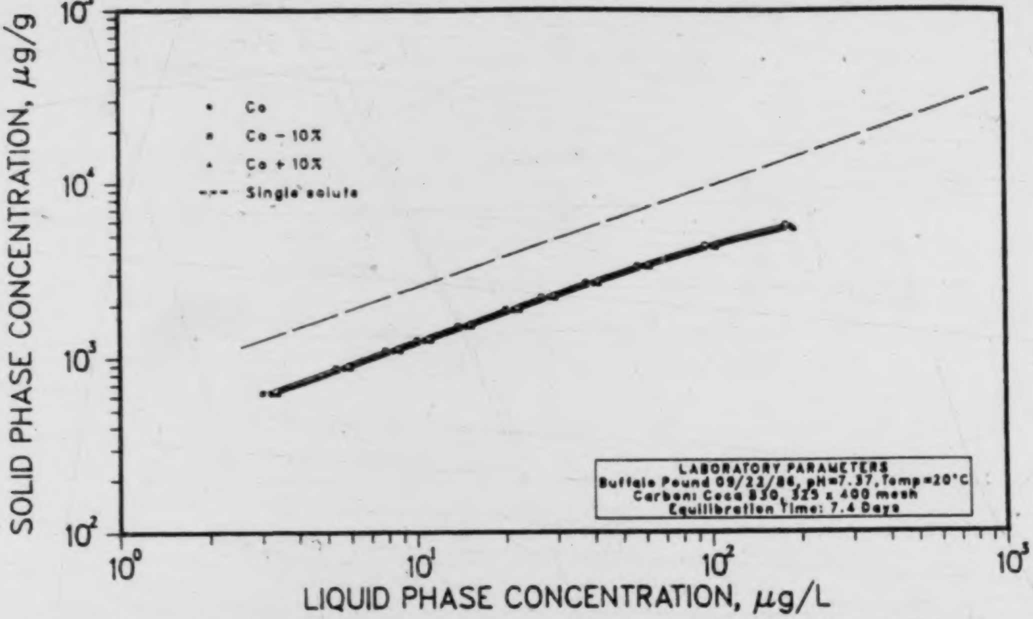


Figure V.63 Effect of Varying C_O by 10% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

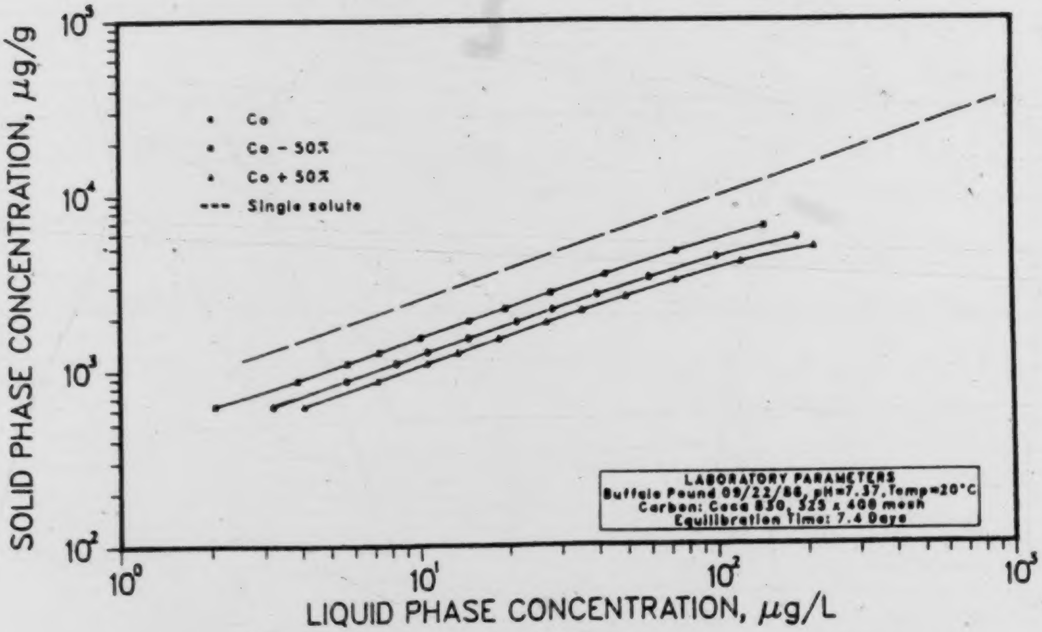


Figure V.64 Effect of Varying C_O by 50% Upon IAST Predictions for Dibromochloromethane Using HC's Fit to Bromodichloromethane

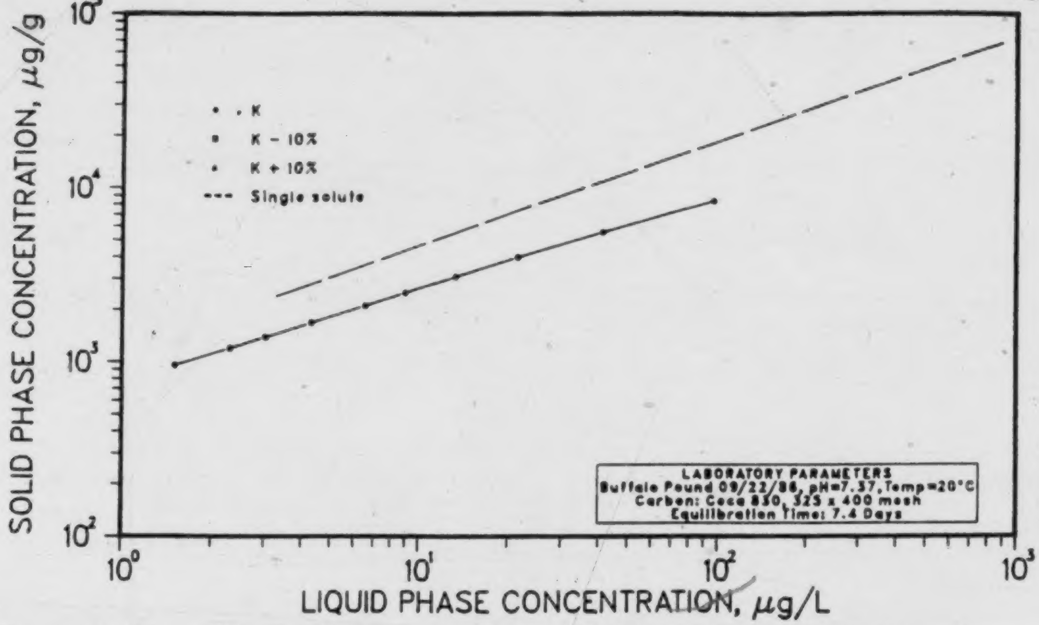


Figure V.65 Effect of Varying K by 10% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

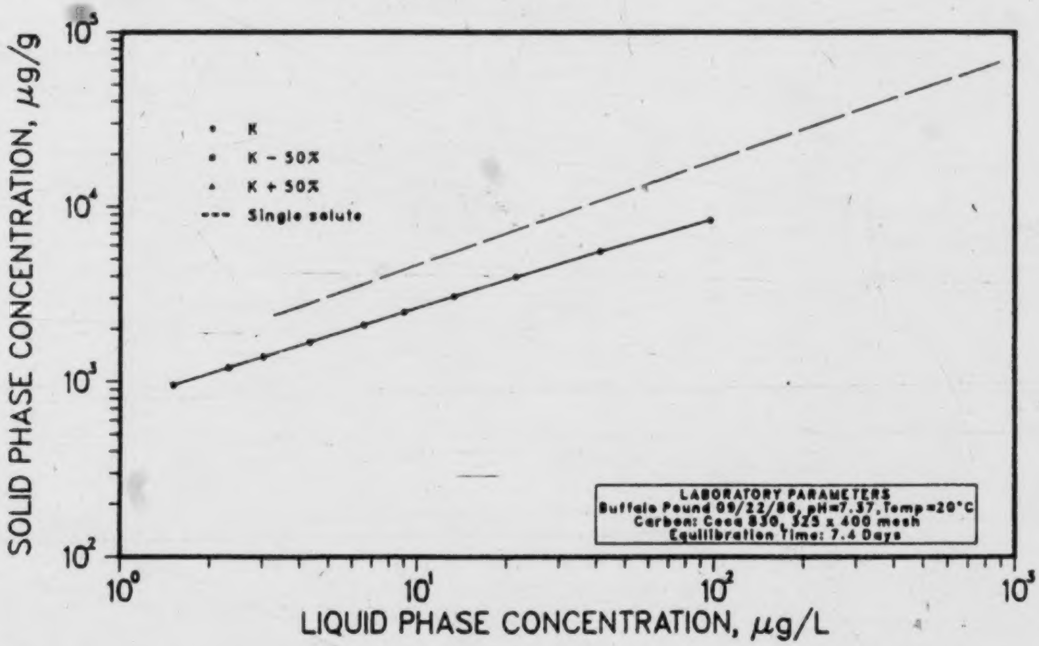


Figure V.66 Effect of Varying K by 50% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

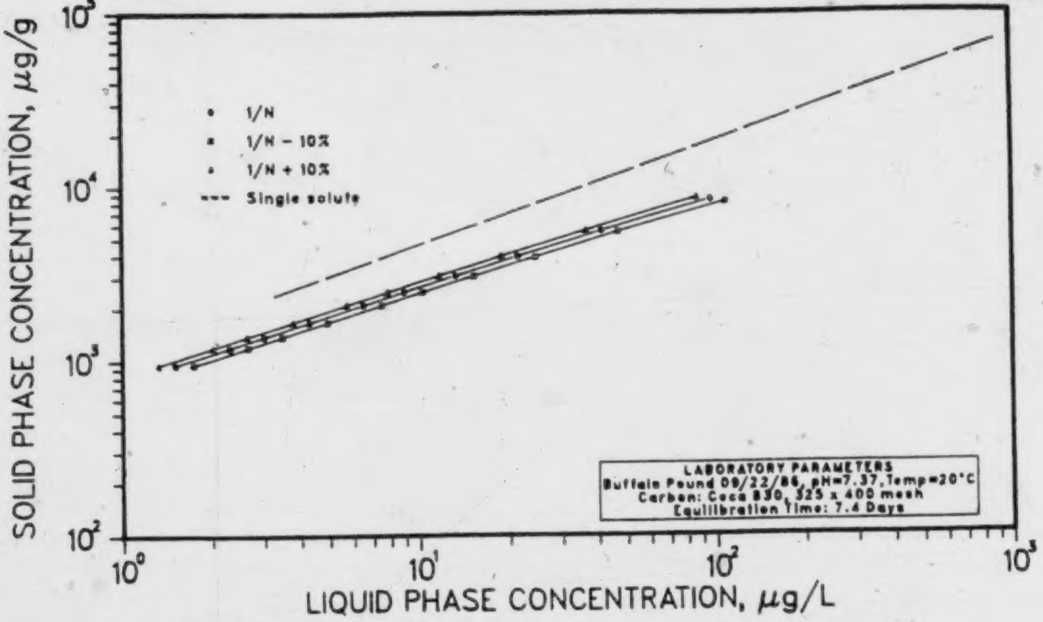


Figure V.67 Effect of Varying 1/n by 10% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

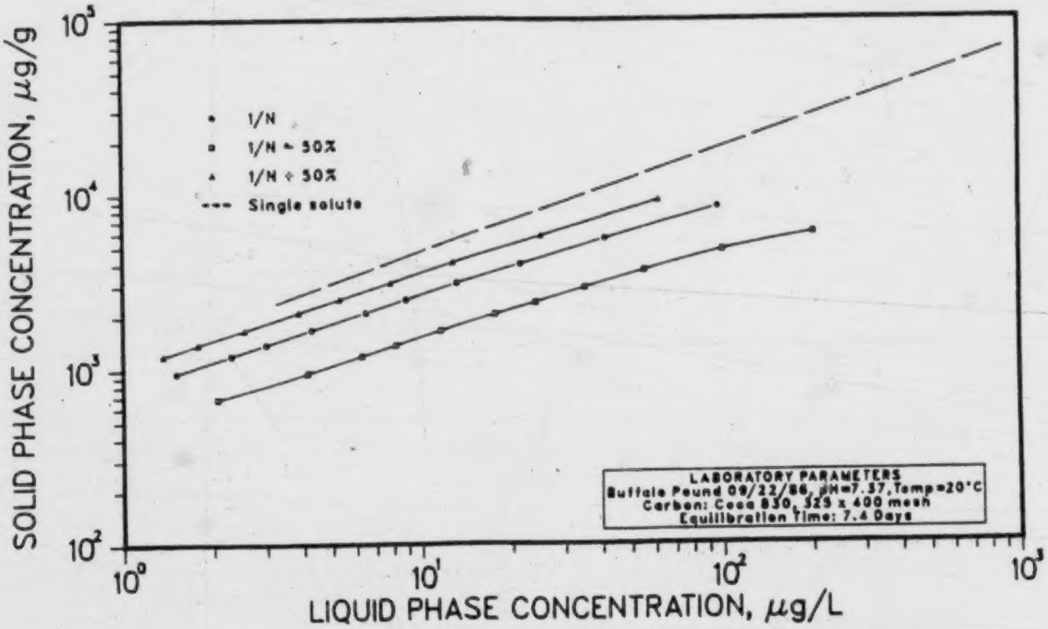


Figure V.68 Effect of Varying 1/n by 50% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

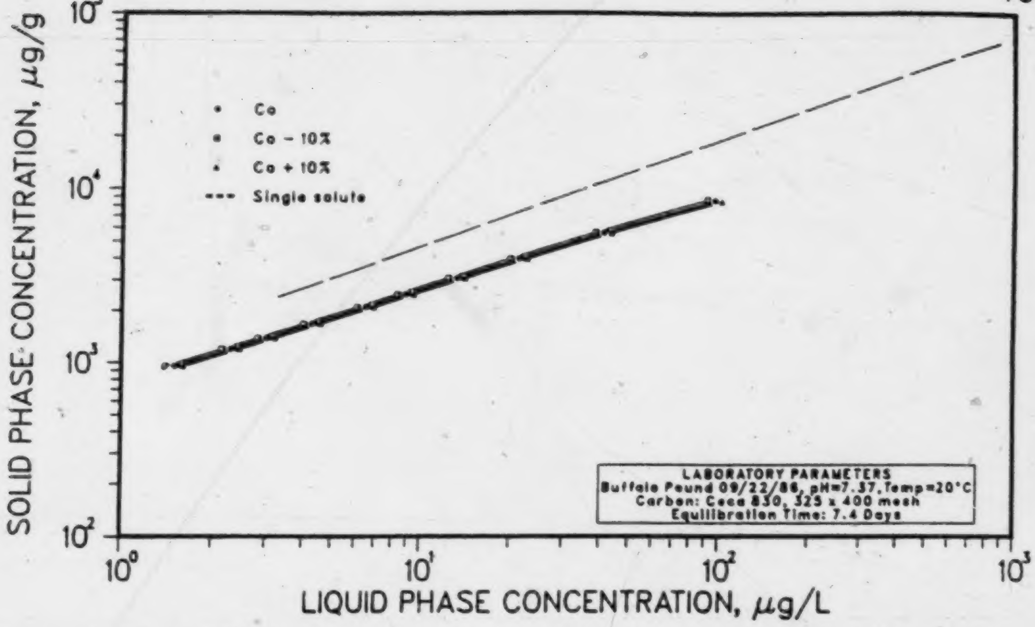


Figure V.69 Effect of Varying C_0 by 10% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

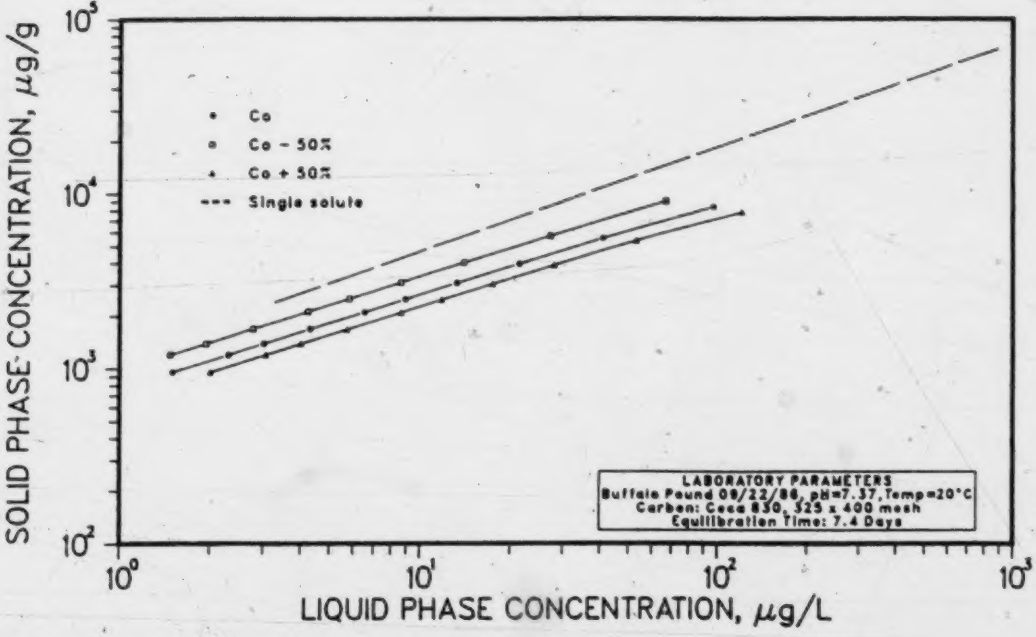


Figure V.70 Effect of Varying C_0 by 50% Upon IAST Predictions for Bromoform Using HC's Fit to Bromodichloromethane

Table V.1 Comparison of APE's for IAST Using Both Averaged and Non-Averaged HC's - 09/22/86 Water Matrix on Ceca 830

Hypothetical Component Properties:

	K $(\mu M/g)(L/\mu M)^{1/n}$	1/n	C_o $(\mu M/L)$
Original	808	0.400	3.81
Averaged	797	0.400	4.02

Compound	Fit/Predicted	APE (%)			
		Original HC's		Averaged HC's	
		C	Q	C	Q
Bromodichloromethane	Fit				
Chloroform	Predicted	23.0	6.62	28.6	5.61
Bromodichloromethane	Predicted	2.15	0.49	7.52	9.74
Dibromochloromethane	Predicted	9.39	0.65	16.7	10.5
Bromoform	Predicted	11.3	0.66	35.3	8.40

Table V.2 Comparison of APE's for IAST Using Both Averaged and Non-Averaged HC's - 10/06/86 Water Matrix on Ceca 830

Hypothetical Component Properties:

	K $(\mu M/g)(L/\mu M)^{1/n}$	1/n	C_o $(\mu M/L)$
Original	792	0.400	4.45
Averaged	797	0.400	4.02

Compound	Fit/Predicted	APE (%)			
		Original HC's		Averaged HC's	
		C	Q	C	Q
Bromodichloromethane	Fit				
Chloroform	Predicted	15.4	9.41	25.9	7.01
Bromodichloromethane	Predicted	2.05	6.61	3.21	0.50
Dibromochloromethane	Predicted	10.5	5.31	11.8	0.66
Bromoform	Predicted	13.1	4.29	24.8	1.65

Table V.3 Comparison of APE's for IAST Using Both Averaged and Non-Averaged HC's - 10/22/86 Water Matrix on Ceca 830

Hypothetical Component Properties:

	K $(\mu M/g)(L/\mu M)^{1/n}$	1/n	C_o $(\mu M/L)$
Original	796	0.400	4.27
Averaged	797	0.400	4.02

Compound	Fit/Predicted	APE (%)			
		Original HC's		Averaged HC's	
		C	Q	C	Q
Bromodichloromethane	Fit				
Chloroform	Predicted	29.4	4.01	12.6	7.62
Bromodichloromethane	Predicted	14.1	0.75	4.74	6.34
Dibromochloromethane	Predicted	7.10	0.28	7.40	4.95
Bromoform	Predicted	NC	NC	34.0	3.05

NC - Not Calculated

Table V.4 Comparison of Carbon Capacity for Chloroform: Hypothetical Components Varied by 10% and 50%

	Carbon Capacity, Q (µg/g) @ C_e = 10 µg/L					
HC Parameter	-10%	0%	+10%	-50%	0%	+50%
K $(\mu M/g)(L/\mu M)^{1/n}$	196	196	196	196	196	196
1/n	196	196	200	118	196	264
C_o (µM/L)	201	196	189	235	196	171

Single Solute Capacity: 403 µg/g (@ C_e = 10 µg/L)

Table V.5 Comparison of Carbon Capacity for Bromodichloromethane: Hypothetical Components Varied by 10% and 50%

	Carbon Capacity, Q (µg/g) @ C_e = 10 µg/L					
HC Parameter	-10%	0%	+10%	-50%	0%	+50%
K $(\mu M/g)(L/\mu M)^{1/n}$	621	621	621	788	621	530
1/n	562	621	743	489	621	728
C_o (µM/L)	646	621	585	788	621	530

Single Solute Capacity: 1312 µg/g (@ C_e = 10 µg/L)

Table V.6 Comparison of Carbon Capacity for Dibromochloromethane: Hypothetical Components Varied by 10% and 50%

	Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L					
HC Parameter	-10%	0%	+10%	-50%	0%	+50%
K (μM/g)(L/μM)$^{1/n}$	1240	1240	1240	1240	1240	1240
1/n	1130	1240	1370	714	1240	1640
C_o (μM/L)	1270	1240	1170	1510	1240	1050

Single Solute Capacity: 2495 μg/g (@ C_e = 10 μg/L)

Table V.7 Comparison of Carbon Capacity for Bromoform: Hypothetical Components Varied by 10% and 50%

	Carbon Capacity, Q (μg/g) @ C_e = 10 μg/L					
HC Parameter	-10%	0%	+10%	-50%	0%	+50%
K (μM/g)(L/μM)$^{1/n}$	2530	2530	2530	2530	2530	2530
1/n	2390	2530	2830	1500	2530	3490
C_o (μM/L)	2807	2530	2590	3360	2530	2260

Single Solute Capacity: 5572 μg/g (@ C_e = 10 μg/L)

Appendix VI

Evaluation of the Effect of Pre-Adsorbed THM'S on Adsorptive Capacity

As described in Section 5.6.4.4, two pre-loaded carbon samples obtained from a pilot study conducted by Huck et al. (1988) were evaluated using isotherm experiments. These experiments were performed by Ramuto Etcheverry and Jean-Pierre Morin who, at the time, were both visiting students from the Ecole Superieure d'Ingenieurs de Poitiers, France. The purpose was to determine the effect of pre-adsorbed THMs on residual capacity for chloroform and bromodichloromethane. Prior to conducting these experiments, a series of isotherms were conducted to evaluate an alternative to the commonly used freeze-drying method of preparing carbon. The objectives of evaluating centrifugation alone as opposed to centrifugation followed by freeze-drying were:

1) To determine if freeze-drying resulted in a loss of pre-loaded organics, including VOCs,
2) To determine if the less time-consuming method of centrifugation alone could be used in lieu of freeze-drying.

A discussion of the preparation methodology is presented first, followed by an evaluation of the impact of pre-loaded THMs on adsorptive capacity.

1. Comparison of Pre-Loaded Carbon Preparation Methods

To compare the use of centrifugation alone, to a combination of centrifugation followed by freeze-drying, chloroform and bromodichloromethane isotherms were conducted using three different carbon samples which were pre-loaded with natural organic matter under a variety of conditions (Figure VI.1). Two of the pre-loaded carbons (Filtrasorb 400®) were obtained following 28 days of pre-loading, from small columns installed in conjunction with a pilot study conducted at the Rossdale water treatment plant, Edmonton (Huck et al., 1988). One stream (chlorine stream) received the addition of approximately 0.26 mg/L free chlorine prior to entering the GAC column. The influent water to the second column (reference stream) consisted of the same conventionally treated drinking water, but without the addition of any disinfectant. The third carbon sample (Filtrasorb 300®) was obtained at a depth of approximately 0.5 m in one of the 3.05 m deep full-scale GAC contactors in service at the Buffalo Pound water treatment plant, Moose Jaw, Saskatchewan. This contactor received conventionally treated pre-chlorinated water which exhibited both high TOC (average 2.6 mg/L) and moderate TTHM concentrations (average 41.4 µg/L). The GAC sample was collected following 60 days of continuous contactor operation.

Centrifugation of carbon samples was conducted using a bench top centrifuge operated for 3 minutes at 3000 rpm. Carbon samples were placed in sintered glass filter funnels which allowed water to be separated from the carbon (suggested by D. Rector, Department of Civil Engineering, University of Alberta). The methods used for

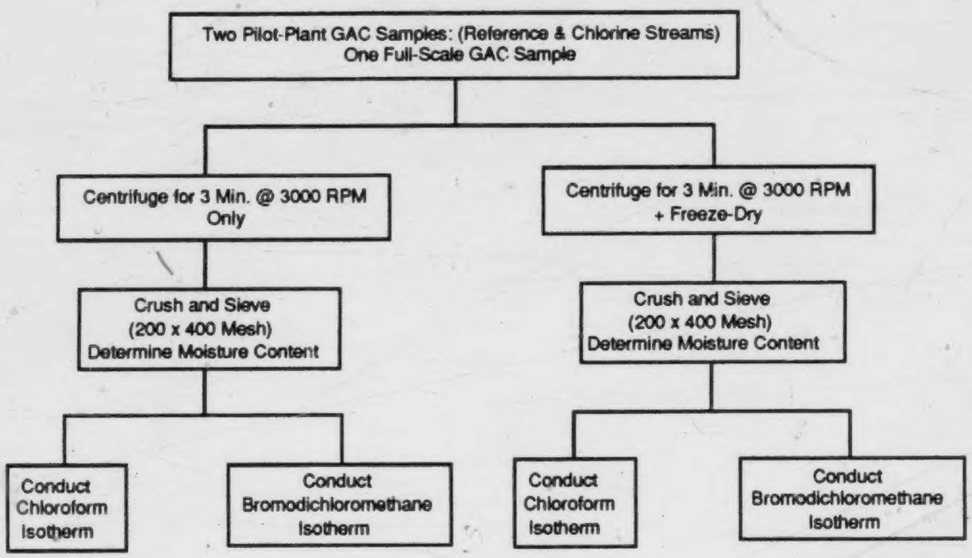

Two Pilot-Plant GAC Samples: (Reference & Chlorine Streams)
One Full-Scale GAC Sample
Centrifuge for 3 Min. @ 3000 RPM
Only
Centrifuge for 3 Min. @ 3000 RPM
+ Freeze-Dry
Crush and Sieve
(200 x 400 Mesh)
Determine Moisture Content
Crush and Sieve
(200 x 400 Mesh)
Determine Moisture Content
Conduct
Chloroform
Isotherm
Conduct
Bromodichloromethane
Isotherm
Conduct
Chloroform
Isotherm
Conduct
Bromodichloromethane
Isotherm

Figure VI.1 Preparation of Pre-Loaded Carbon for Chloroform and Bromodichloromethane Isotherm Experiments

subsequent freeze-drying and crushing/sieving are presented in Appendix I. Isotherm results for various pre-loaded carbons which show the effect of different preparation methods are presented in Tables VI.1 and VI.2 for chloroform and bromodichloromethane, respectively. Confidence intervals (95% confidence level) for Freundlich K and 1/n parameter values obtained using both reference and chlorine stream pre-loaded carbon, were observed to overlap in all cases, indicating that the isotherm parameters were not statistically different and therefore that the carbon preparation method did not have a significant effect on isotherm results. Wider variations in K and 1/n parameter values were observed for both chloroform and bromodichloromethane isotherms when using the pre-loaded Buffalo Pound carbon. This carbon had been pre-loaded for a longer period of time and with higher influent concentrations of TOC and TTHMs than the pilot plant carbon with chloroform representing approximately 70% of the TTHM concentration. The higher capacity observed for chloroform following freeze-drying suggests that some VOCs were lost during carbon preparation. Although confidence intervals overlapped for bromodichloromethane, the higher capacity following freeze-drying also suggests that some VOCs were removed during carbon preparation.

The aforementioned isotherm experiments were conducted following completion of THM pre-loading isotherm investigations but prior to MX isotherm studies, therefore the freeze-drying method used by other workers (Crittenden, 1986) was used for all THM isotherm investigations whereas carbon prepared for MX studies involved using only the centrifugation procedure.

Table VI.1 Comparison of Preloaded Carbon Preparation Methods Using Chloroform Isotherm Results

GAC Source	K $(\mu M/g)(L/\mu M)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval
Pilot-Plant Reference [a]				
Centrifuged	75.8	55.2-96.6	0.678	0.641-0.715
Centrifuged+F.Dried	32.5	2.2-62.8	0.768	0.643-0.89
Pilot-Plant Chlorine [a]				
Centrifuged	29.0	2.36-55.6	0.788	0.666-0.911
Centrifuged+F.Dried	39.3	1.24-77.4	0.749	0.618-0.880
Full-Scale Contactor [b]				
Centrifuged	3.8	-13.1-20.7	1.03	0.48-1.58
Centrifuged+F.Dried	192.9	-86.8-473	0.48	0.28-0.68

*NLLS: Non-Linear Least Squares

(a) Filtrasorb 400® carbon removed from a preloading column, installed at the Rossdale pilot-plant, following 28 days of operation

(b) Filtrasorb 300® carbon removed from top 0.5 m of a full-scale contactor at the Buffalo Pound water treatment plant, following 60 days of operation

Table VI.2 Comparison of Preloaded Carbon Preparation Methods Using Bromodichloromethane Isotherm Results

GAC Source	K $(\mu M/g)(L/\mu M)^{1/n}$ NLLS Fit*	95% Confidence Interval	1/n NLLS Fit*	95% Confidence Interval
Pilot-Plant Reference [a]				
Centrifuged	211.5	117.5-305.5	0.597	0.542-0.653
Centrifuged+F.Dried	212.3	106.9-317.6	0.591	0.529-0.653
Pilot-Plant Chlorine [a]				
Centrifuged	65.0	-0.656-130.6	0.763	0.632-0.894
Centrifuged+F.Dried	63.7	8.81-118.7	0.766	0.653-0.879
Full-Scale Contactor [b]				
Centrifuged	13.4	-6.7-33.6	0.900	0.718-1.08
Centrifuged+F.Dried	40.1	-9.4-89.5	0.789	0.634-0.944

*NLLS: Non-Linear Least Squares

(a) Filtrasorb 400® carbon removed from a preloading column, installed at the Rossdale pilot-plant, following 28 days of operation

(b) Filtrasorb 300® carbon removed from top 0.5 m of a full-scale contactor at the Buffalo Pound water treatment plant, following 60 days of operation

Recent investigations by Speth (1989) compared cis-1,2-dichloroethene isotherms conducted using pre-loaded carbons which were prepared by; 1) drying under vacuum followed by further drying with a dessicant, 2) crushing the carbon while it was wet and 3) washing the carbon with water prior to applying methods (1) or (2). He reported no difference in subsequent isotherm results, based on visual interpretation, with respect to the carbon preparation method employed.

2. Effect of Pre-Adsorbed THMs on Adsorptive Capacity

To evaluate the effect of pre-adsorbed VOCs (including THMs) on isotherm capacity, Freundlich parameters were compared for chloroform and bromodichloromethane using both the reference stream and chlorine stream pre-loaded GAC. Results are shown in Tables VI.1 and VI.2. When Freundlich parameters for chloroform isotherms conducted using carbon (freeze-dried) from the two streams are compared, the observed values are almost identical. For bromodichloromethane the reference stream carbon exhibited a slightly higher capacity than the chlorine stream carbon however 95% confidence intervals were shown to overlap. Isotherm results for chloroform and bromodichloromethane plotted in Figures VI.2 and VI.3, respectively, allow visual comparison and show that the effect of pre-adsorbed VOCs (including THMs) is not significant. It should be noted that the carbon used for this comparison was not obtaied from Buffalo Pound, the plant used for THM pre-loading studies. A larger reduction in capacity due to pre-adsorbed THMs would be expected for the Buffalo Pound pre-loaded carbon where TTHM concentrations averaged 48.9 µg/L, compared to 11.0 µg/L at the Rossdale pilot plant.

Similar pre-loaded carbon isotherm studies involving trichloroethene (TCE) are reported by Hand et al. (1989). Isotherms for TCE were conducted with carbon obtained from the top, middle and bottom of a full-scale adsorber following approximately one year of operation. The average TOX reported for the influent water was 141.0 µg/L. The authors report that although the GAC contained some TCE, the reduction in capacity was due to natural organic matter. It was assumed that for the average TCE influent concentration of 47.9 µg/L, the capacity reduction attributable to pre-adsorbed TCE would be negligible compared with capacities observed in isotherm tests.

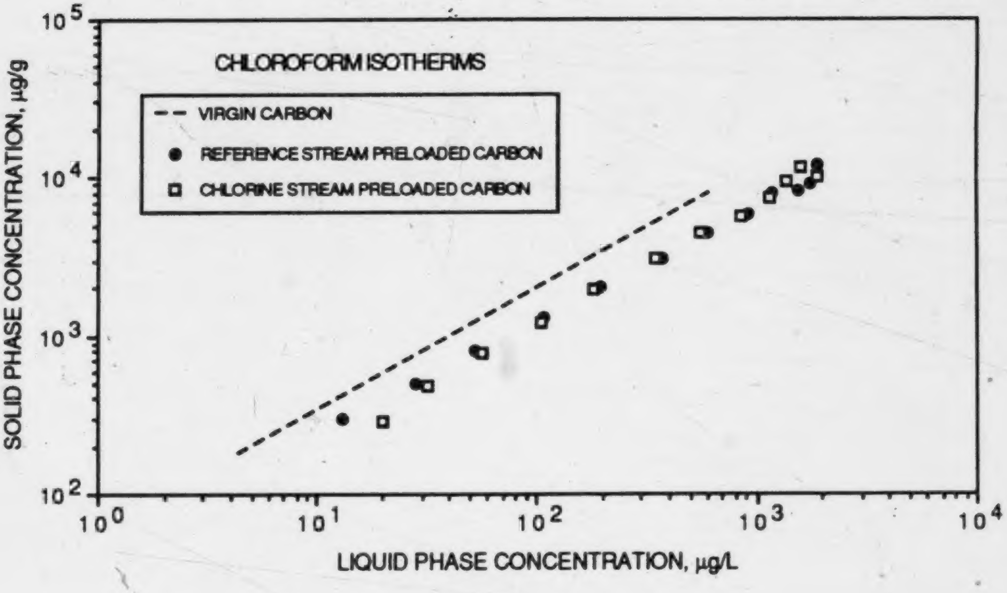


Figure VI.2 Chloroform Isotherms Obtained Using Freeze-Dried, Pre-Loaded Carbon (Chlorine and Reference Streams)

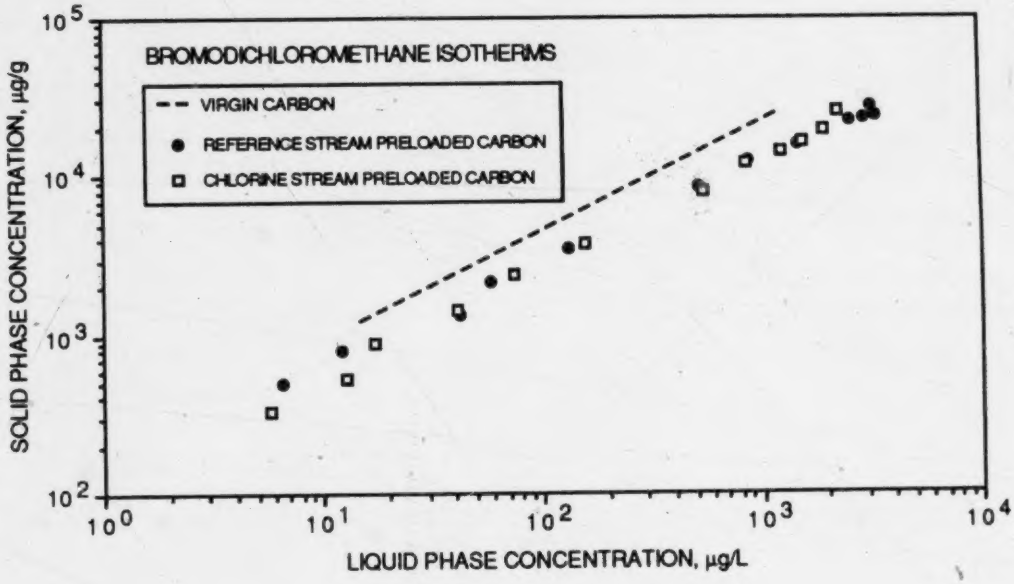


Figure VI.3 Bromodichloromethane Isotherms Obtained Using Freeze-Dried, Pre-Loaded Carbon (Chlorine and Reference Streams)

Appendix VII

Thermal Desorption Investigations

Thermal Desorption Analyses

In an attempt to quantify THM's adsorbed on pre-loaded carbon, steps towards method development were undertaken to allow THM's to be thermally desorbed from carbon samples prior to GC analysis. The initial purpose of developing this methodology was to measure THM's adsorbed on carbon used in the pre-loading column installed at the Buffalo Pound water treatment plant. The purpose of pre-loading this carbon was to quantify reduction in THM adsorption capacity due to slowly adsorbing background organics. In order to quantify this effect it was necessary to separate out the effect of capacity reduction due to the presence of co-adsorbed THM's. Development of a thermal desorption method could have also be applied to quantify THM's adsorbed on carbon samples obtained at various depths from the full-scale GAC beds at Buffalo Pound. Finally, thermal desorption analyses could be used to provide a check on the loss of volatiles attributable to freeze drying, the method commonly used to prepare pre-loaded carbon for isotherm experiments.

Unfortunately, because of time constraints this method could not be brought to fruition during the course of this study; the development steps undertaken and associated preliminary results are described in this section.

Initially a set of experiments were designed to allow; (a) optimization of method precision and (b) determination of the accuracy of instrumental measurements. To assist in this evaluation procedure, a series of carbon-THM "standards" were prepared. In an experiment designed using IAST, a series of virgin carbon samples were pre-loaded with known amounts of THM's in a four component organic free water background matrix such that an approximately equal amount of each component was adsorbed. Actual amounts of individual THM components adsorbed on the carbon samples are shown in Table VII.1. These samples served as "standards" to permit calibration and verification of THM desorption procedures.

To provide a check on the loss of volatiles attributable to the freeze drying procedure, one of the pre-loaded carbons (sample 5) was subdivided during preparation as shown on Figure VII.1. Using these sub-samples, THM's adsorbed on the carbon could be evaluated prior to freeze-drying, following freeze-drying, and following the crushing and sieving steps. Following each step, moisture content was determined such that loadings could be expressed on a dry weight basis.

As an alternative to the freeze drying method of dewatering a portion of the carbon was subjected to centrifugation prior to crushing and sieving. This method differed from freeze-drying in that it was conducted at ambient temperatures and did not incorporate vacuum pressures. Use of centrifugation may serve as an alternate method of dewatering carbon samples and therefore simplify carbon preparation for use in isotherm experiments. A comparison of centrifugation vs freeze-drying would also show which method is preferable in minimizing the loss of volatiles during carbon preparation.

Table VII.1 Pre-Loaded Carbon Standards

Sample Number	Loading on Carbon (µg/g)[a]			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
1	867.8	700.9	948.2	919.1
2	439.0	351.4	474.7	458.9
3	894.3	651.1	731.8	969.1
4	88.2	70.4	95.2	92.4
5	90.3	65.3	73.3	97.2

[a] As defined by liquid phase calculations

Note: Sample 5 was dewatered according to the various methods shown on the Figure VII.1. This sample allowed the various preparation procedures to be evaluated in terms of THM loss. All other samples were freeze-dried and crushed. These samples served as calibration standards

Samples: 4, 2 and 1 roughly provided standards of 100 µg/g, 500 µg/L and 1000 µg/g. Sample 1 served as a close duplicate to 3.

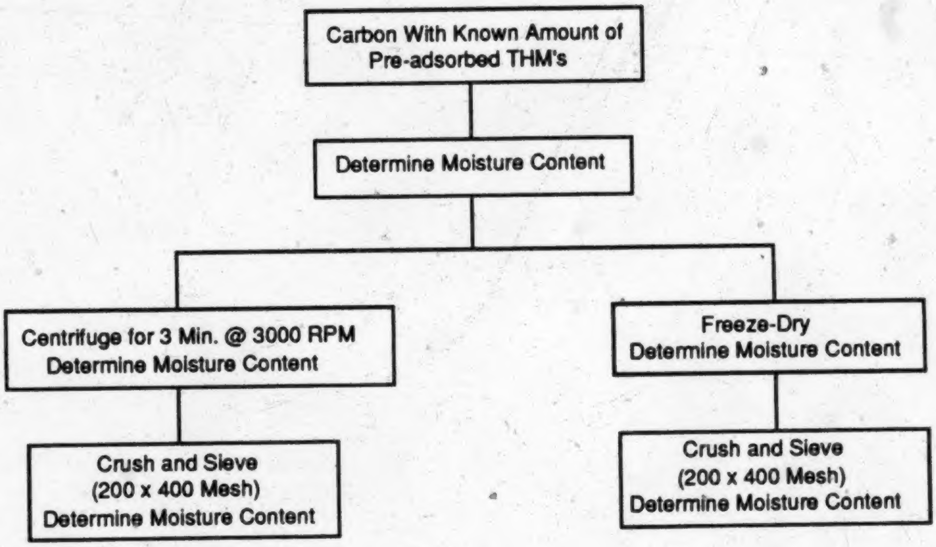

Carbon With Known Amount of Pre-adsorbed THM's
Determine Moisture Content
Centrifuge for 3 Min. @ 3000 RPM Determine Moisture Content
Freeze-Dry Determine Moisture Content
Crush and Sieve (200 x 400 Mesh) Determine Moisture Content
Crush and Sieve (200 x 400 Mesh) Determine Moisture Content

Figure VII.1 Preparation of Samples for THM Analyses To Compare Freeze-Dried vs Centrifuged Standards

1. Preliminary Thermal Desorber/GC Operating Conditions

To provide an estimate of relative THM retention times, 2 µL of a known mixture of trihalomethane standards was injected into an Envirochem Inc. Thermal Tube Desorber Model 850. The mixture was then thermally desorbed for 2 minutes at 150°C directly onto the head of a capillary column (30 m x 0.32 mm; DB-WAX-30W; HP 5890A GC; FID detector) and held for 2 minutes at 20°C. The GC oven was temperature programmed to 150°C at a rate of 10°C/min and then to a temperature of 200°C at a rate of 20°C/min and held for 5 minutes at that temperature. A chromatogram of the trihalomethane standard is shown in Figure VII.2. The peaks eluting at 6.76 min, 8.82 min, 10.55 min, and 12.88 min had been earlier identified by individual retention times as $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ respectively.

A sample of powdered carbon was then subjected to the same analysis conditions to determine if trihalomethanes could be successfully desorbed. The sample chosen for initial investigations (sample 5) had been previously pre-loaded with trihalomethanes in organic-free water, dewatered by centrifugation and crushed to a < 400 mesh fraction. Results for a sample weight of approximately 0.1 g are shown in Figure VII.3. These chromatograms show the effect of initially desorbing at 150°C for 2 minutes then re-desorbing the same sample at 250°C (2 min) and 350°C (2 min). Alben et al. (1983) reported using a temperature of 250°C for

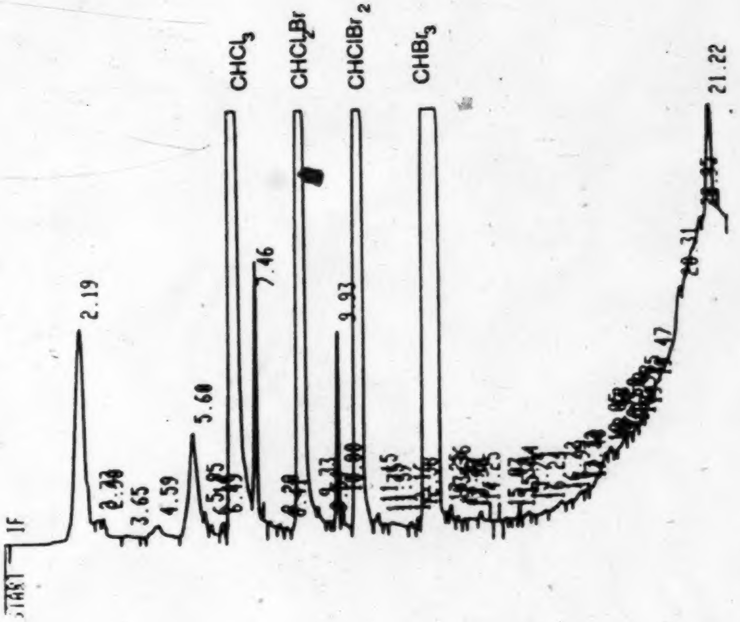


Figure VII.2 Chromatogram of Four Component Trihalomethane Standard Using Thermal Desorption at 150°C

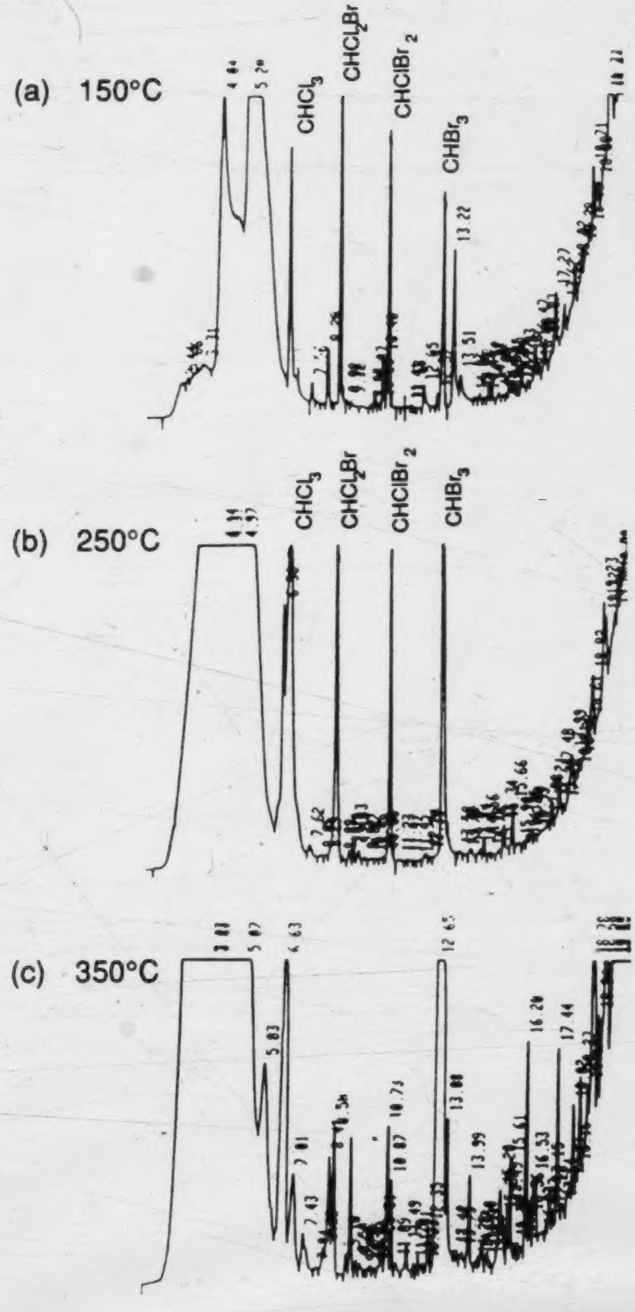


Figure VII.3 Chromatograms For Pre-loaded Activated Carbon (Centrifuged) Desorbed At Three Different Temperatures

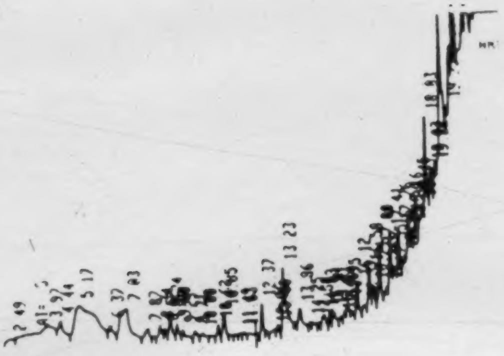
desorption of chloroform from activated carbon. From these preliminary results an optimal desorption temperature would appear to be at or slightly above 250°C.

To provide a preliminary comparison of trihalomethanes remaining on centrifuged vs freeze-dried carbon a sample of freeze-dried carbon was analyzed using the conditions mentioned above. The sample chosen (sample 1) had been pre-loaded to yield a solid phase concentration of approximately ten times the concentration on the previously analyzed centrifuged samples. Chromatograms produced following desorption at three different temperatures are shown in Figure VII.4. Peak heights appear much lower than those reported for the centrifuged carbon especially at the 150°C desorb temperature. The large solvent peak present at the start of the centrifuged carbon chromatograms however appears much higher than in similar freeze-dried results. This suggests that trihalomethanes may possibly be lost as a result of water removed during the freeze-drying process. Replicate analyses however would be required to confirm these observations.

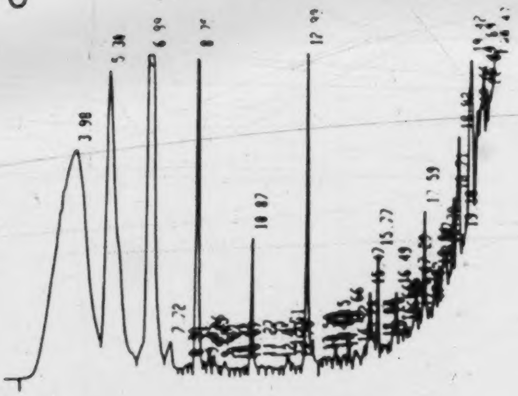
2. Selection of Internal Standard

A decision was made to incorporate an internal standard into each run to correct for the drift in retention times attributable to flowrate changes caused by variations in packing individual desorber tubes with powdered carbon. Headspace from many different solvents was injected into the desorber in an attempt to find an internal standard with a retention time that would fall within the window of the four trihalomethanes.

(a) 150°C



(b) 250°C



(c) 350°C

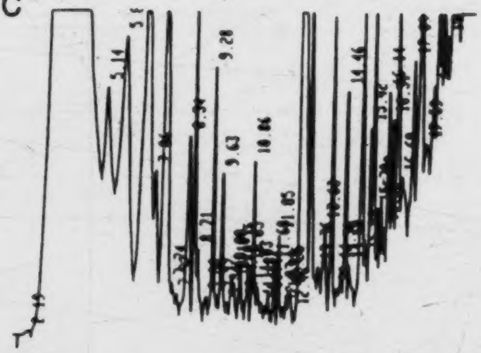


Figure VII.4 Chromatograms For Pre-loaded Activated Carbon (Freeze-dried) Desorbed At Three Different Temperatures.

The chemicals p-dichloro-benzene and m-chlorotoluene both produced acceptable retention times, however these times were found to vary inversely with respect to the amount of water that was injected at the same time. Since it was known water would be present when carbon samples were desorbed it was imperative that the internal standard not be influenced by this phenomena. For this reason and to eliminate change-over of GC capillary columns, all further work was conducted using a 30 m x 0.32 mm, SPB-5 column. Since this column was less polar in nature a temperature program for the GC was selected such that it would begin at a lower temperature. The GC oven was programmed as follows: initial hold at -30°C for 2 minutes, ramp at 10°C/min to 150°C, then to 200°C at 20°C/min. The higher temperature served as a cleanout and was not used in every run. The desorber temperature was set to 250°C for 2 minutes. Chromatographic results from an initial run produced four well defined peaks. As before, retention times for individual THM components were defined by single standard headspace injections. It should be stressed that these results represented the initial steps of method development and were not meant to be quantitative. The next step in this work would be to identify a suitable internal standard. Once this has been completed, placement of the internal standard should be examined. As a first trial 1 µL or 2 µL of the standard should be placed on the inner wall of the desorption tube immediately downstream of the carbon sample to avoid problems associated with adsorption and desorption of the internal standard from the carbon.

A method should also be investigated to minimize the amount of a desorbed water vapour reaching the GC column and thus reduce the possibility of damage at sub-freezing temperatures. The use of a Tenax® trap should be investigated first. Using this method, volatiles would first be desorbed from the carbon onto the Tenax®. It is anticipated that by incorporating this intermediate step water vapour would be vented to atmosphere and not reach the GC column. The volatiles trapped on the Tenax® would then be desorbed onto the head of the GC column.

Following completion of these method development steps, desorption operating parameters should be optimized and carbon samples analyzed to further evaluate the dewatering preparation methods of freeze-drying vs centrifugation.

Appendix VIII

Buffalo Pound Water Treatment Plant Water Quality Data

Table VIII.1 Raw Water Quality Data - 1986

				Monthly Average			
Parameters	Units	June	July	Aug	Sept	Oct	Nov
PHYSICAL							
Colour (Apparent)	Pt/Co	16	14	21	20	13	9
Conductivity	umhos/cm	490	472	447	490	492	510
Diss. Oxygen	mg/L	8.6	8.4	8.1	8.0	8.2	10.0
Diss. Solids	mg/L	399	386	358	383	397	416
Odour	T.O.N.	14	16	40	28	26	22
Particles (x 1000)	per 10 mL	118	84	176	110	59	71
pH	pH units	8.2	8.3	8.5	7.8	7.9	8.0
Suspend. Solids	mg/L	4.6	5.1	10.2	5.1	4.6	3.4
Temperature	Deg. C	18.0	19.0	19.0	13.0	8.6	2.0
Turbidity	NTU	2.4	2.1	6.1	2.8	2.2	2.1
MAJOR CONSTITUENTS							
Alkalinity (p)	mg/L $CaCO_3$	0	1	1	0	0	0
Alkalinity (total)	mg/L $CaCO_3$	159	152	133	141	145	154
Bicarbonate	mg/L	194	183	160	172	177	189
Calcium	mg/L	42	40	32	37	39	41
Carbon Dioxide	mg/L	1	1	0	5	6	3
Carbonate	mg/L	0	1	1	0	0	0
Chloride	mg/L	10	10	11	11	10	11
Hardness (total)	mg/L $CaCO_3$	185	179	158	173	175	183
Magnesium	mg/L	18	19	18	19	20	20
Potassium	mg/L	4.5	4.3	4.5	4.8	4.6	4.9
Sodium	mg/L	36	37	37	40	39	41
Sulphate	mg/L	92	92	93	103	107	110
TRACE CONSTITUENTS							
Aluminum (diss)	mg/L	.40	.38	.34	.38	.25	.45
Aluminum (total)	mg/L	.67	.68	.60	.62	.46	.63
Ammonia N	mg/L N	.08	.06	.07	.06	.06	.09
BOD (5-day)	mg/L	1.4	1.7	3.8	3.0	2.7	2.8
Chlorophyll a	µg/L	5	6	40	19	15	9
Cyanide	µg/L	<10	<10	<10	<10	<10	<10
COD	mg/L	14	15	19	17	17	18
Detergents	µg/L	<5	<5	<5	<5	<5	<5
Fluoride	mg/L	.18	.19	.21	.20	.19	.19
Iron (diss)	mg/L	.02	.04	.03	.02	.03	.04
Iron (total)	mg/L	.19	.28	.19	.22	.18	.31
Manganese	mg/L	.03	.04	.05	.03	.01	.01
Nitrate/Nitrite	mg/L N	.02	.02	.16	.37	.37	.41

Table VIII.1 Raw Water Quality Data - 1986 (continued)

		Monthly Average					
Parameters	Units	June	July	Aug	Sept	Oct	Nov
Org N (Kjeldahl)	mg/L N	.41	.41	.65	.53	.53	.44
Org Carbon (diss)	mg/L C	5.0	5.3	5.2	4.6	4.4	4.3
Org Carbon (total)	mg/L C	6.3	6.1	-	-	-	-
Phenols	µg/L	3	4	6	8	9	3
Phosphate (ortho)	µg/L P	2	8	2	4	2	<2
Phosphate (total)	µg/L P	77	61	62	77	43	39
Silica	mg/L	1.2	1.6	1.8	2.8	2.9	2.4
Sulphide	µg/L	<75	<75	<75	<75	<75	<75
Trihalomethanes	µg/L	3	<1	1	1	1	1
BIOLOGICAL							
Algae (x 10^{-6})	per Litre	<.4	<.4	.7	<.4	.8	<.4
Major Algae				BLGR		FLAG	
Crustaceans	per Litre	9	13	10	26	21	20
Nematodes	per Litre	<1	<1	<1	<1	<1	<1
Rotifiers (x 10^{-3})	per Litre	4	1	1	1	<1	<1
BACTERIOLOGICAL							
Actinomycetes	in 100 mL	<100	<100	POSS	<100	<100	POSS
Coliforms (MF)	in 100 mL	2	2	<100	165	11	2
Fecal Coli (MF)	in 100 mL	1	1	12	28	5	1
Fecal Strep	in 100 mL	10	600	880	39	<10	<10
Std. Plate Count	in 1 mL	62	160	722	472	76	96
Sulphur Bacteria		-	-	-	-	-	-
CHEMICAL DOSES							
Alum	mg/L	60	60	67	56	50	50
Pre-Chlorine	mg/L	3.3	2.6	3.7	3.1	2.9	3.5
Post-Chlorine	mg/L	.5	1.1	1.3	1.3	1.2	.2
Fluoride (MJ)	mg/L	.85	.82	.91	.92	.81	.85
Polymer	mg/L	.1	.1	.1	.1	.1	.1
Soda Ash	mg/L	19	16	22	22	16	8
Free Chlorine Residual ex plant	mg/L	1.0	.9	1.0	1.0	.9	.9

Note: Algae Identification, Actinomycetes
FLAG = Flagellate BLGR = Blue-Green POSS = Possible

After Buffalo Pound Operating Data (1986)

Table VIII.2 Treated (Post-GAC) Water Quality Data - 1986

		Monthly Average					
Parameters	Units	June	July	Aug	Sept	Oct	Nov
PHYSICAL							
Colour (Apparent)	Pt/Co	<5	<5	<5	<5	<5	<5
Conductivity	umhos/cm	545	528	507	550	555	565
Diss. Oxygen	mg/L	-	-	-	-	-	-
Diss. Solids	mg/L	431	411	389	413	418	420
Odour	T.O.N.	4	4	6	6	4	7
Particles (x 1000)	per 10 mL	322	132	697	650	177	330
pH pH units	7.3	7.2	7.2	7.3	7.3	7.2	
Suspend. Solids	mg/L	.1	.1	.3	.1	.7	.5
Temperature	Deg. C	-	-	-	-	-	-
Turbidity	NTU	.07	.09	.11	.13	.10	.13
MAJOR CONSTITUENTS							
Alkalinity (p)	mg/L $CaCO_3$	0	0	0	0	0	0
Alkalinity (total)	mg/L $CaCO_3$	148	139	117	129	132	133
Bicarbonate	mg/L	181	169	143	158	161	163
Calcium	mg/L	43	40	32	37	38	40
Carbon Dioxide	mg/L	13	12	12	9	10	12
Carbonate	mg/L	0	0	0	0	0	0
Chloride	mg/L	13	13	15	14	14	13
Hardness (total)	mg/L $CaCO_3$	185	178	158	173	175	183
Magnesium	mg/L	18	19	19	19	19	20
Potassium	mg/L	4.7	4.3	4.7	5.0	4.7	5.0
Sodium	mg/L	46	43	48	49	46	43
Sulphate	mg/L	124	122	127	133	133	133
TRACE CONSTITUENTS							
Aluminum (diss)	mg/L	.35	.33	.33	.36	.26	.46
Aluminum (total)	mg/L	.42	.50	.38	.43	.49	.63
Ammonia N	mg/L N	.07	.06	.07	.05	.05	.06
BOD (5-day)	mg/L	-	-	-	-	-	-
Chlorophyll a	µg/L	<1	<1	-	-	-	-
Cyanide	µg/L	<10	<10	<10	<10	<10	<10
COD	mg/L	4	2	2	6	5	10
Detergents	µg/L	<5	<5	<5	<5	<5	<5
Fluoride	mg/L	.19	.19	.21	.21	.14	.14
Fluoride (MJ)	mg/L	.81	.84	.82	.97	.99	.93
Iron (diss)	mg/L	.02	.02	.02	.02	.03	.03
Iron (total)	mg/L	.02	.02	.07	.08	.07	.19
Manganese	mg/L	.01	.01	.01	.01	.01	.01
Nitrate/Nitrite	mg/L N	.02	.02	.12	.40	.18	.40
Org N (Kjeldahl)	mg/L N	.24	.20	.26	.18	.19	.26

Table VIII.2 Treated (Post-GAC) Water Quality Data - 1986 (continued)

Parameters	Units	June	July	Aug	Sept	Oct	Nov
		Monthly Average					
Org Carbon (diss)	mg/L C	1.9	.7	1.1	1.2	1.5	2.4
Org Carbon (total)	mg/L C	-	-	-	-	-	-
Phenols	µg/L	<2	<2	3	2	3	<2
Phosphate (ortho)	µg/L P	52	20	9	4	<2	<2
Phosphate (total)	µg/L P	48	32	16	7	8	<2
Silica	mg/L	1.6	1.7	2.1	3.0	3.1	2.6
Sulphide	µg/L	<75	<75	<75	<75	<75	<75
Trihalomethanes	µg/L	41	7	22	23	23	34
BIOLOGICAL							
Algae	per Litre	15	8	***	374	<1	<1
Major Algae		DIAT	BLGR	BLGR	BLGR	-	-
Crustaceans	per Litre	<1	<1	<1	<1	<1	<1
Nematodes	per Litre	<1	<1	<1	<1	<1	<1
Rotifiers (x 10^{-3})	per Litre	<1	<1	<1	<1	<1	<1
BACTERIOLOGICAL							
Actinomycetes	in 100 mL	<10	<10	<10	<10	<10	<10
Coliforms (MF)	in 100 mL	<1	<1	<1	<1	<1	<1
Fecal Coli (MF)	in 100 mL	<1	<1	<1	<1	<1	<1
Fecal Strep	in 100 mL	<10	<10	<10	<10	<10	<10
Std. Plate Count	in 1 mL	<1	<10	<10	<10	10	10

Note: Algae counts asterisked (***) were
August 34,000/litre

DIAT = Diatom BLGR = Blue-Green

After Buffalo Pound Operating Data (1986)

Appendix IX

Equilibrium Column Model Predictions

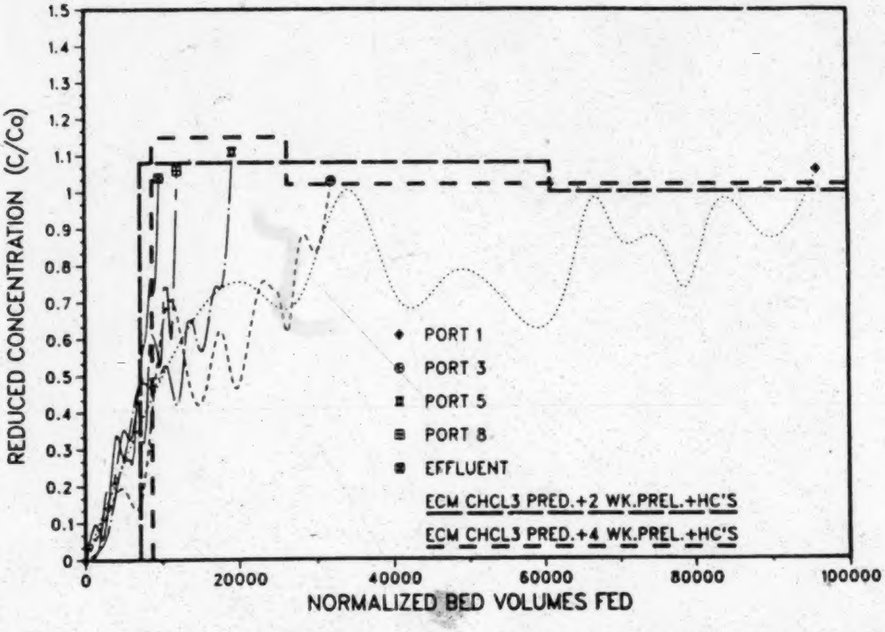


Figure IX.1 Effect of Variable Pre-Loading Time (2 and 4 Weeks) on ECM Prediction of Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

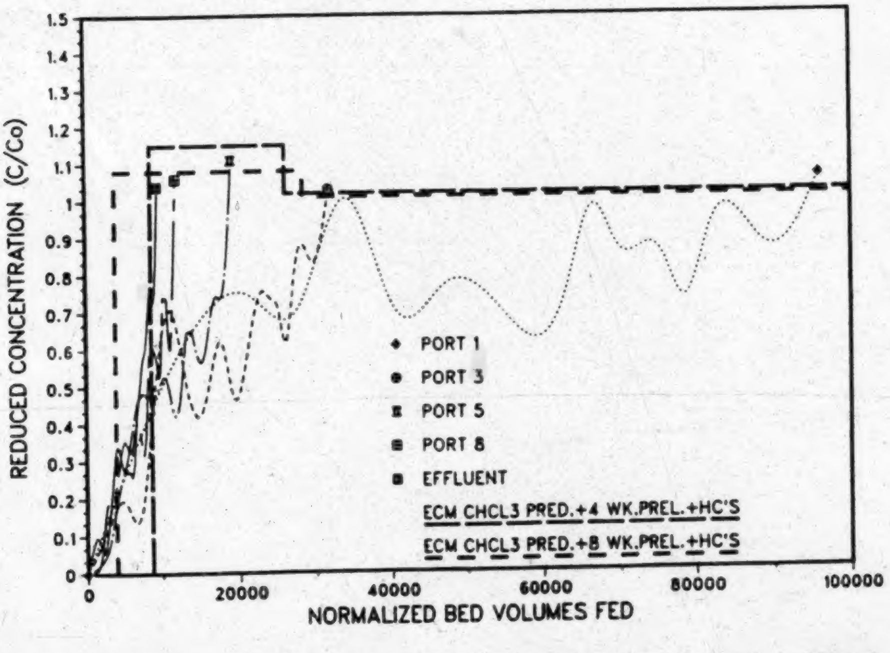


Figure IX.2 Effect of Variable Pre-Loading Time (4 and 8 Weeks) on ECM Prediction of Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

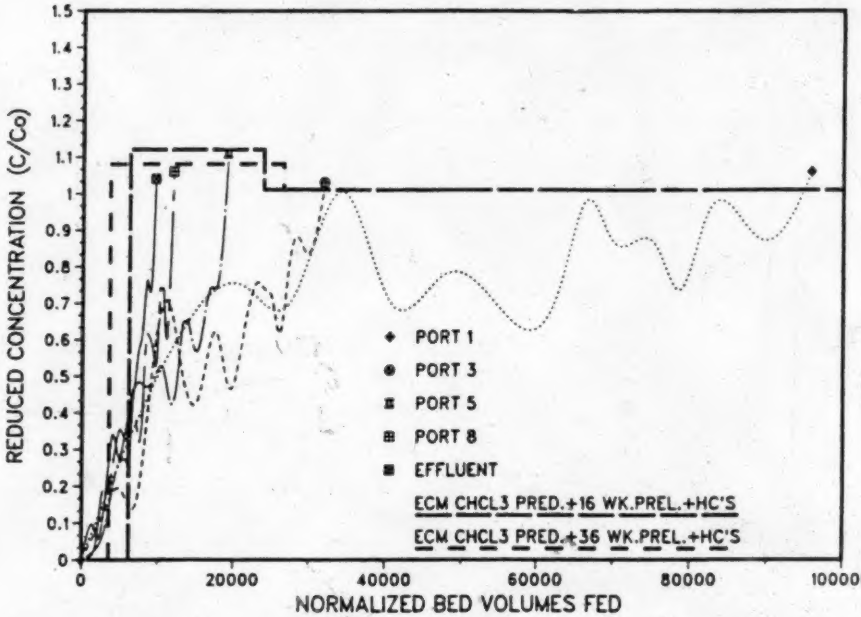


Figure IX.3 Effect of Variable Pre-Loading Time (16 and 36 Weeks) on ECM Prediction of Chloroform Breakthrough (1986 Ceca 830 Ported Bed)

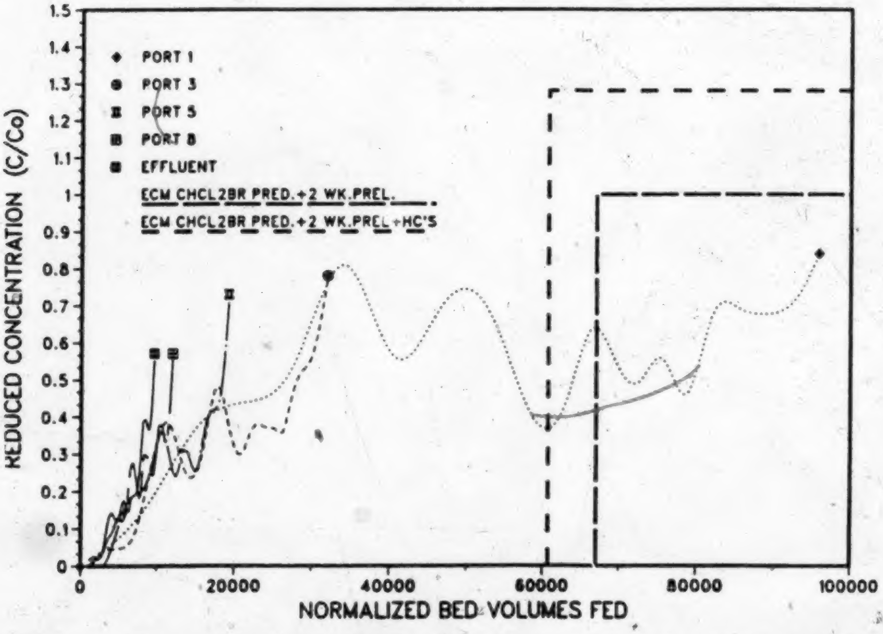


Figure IX.4 Effect of Variable Pre-Loading Time and HCs on ECM Prediction of Bromodichloromethane (1986 Ceca 830 Ported Bed)

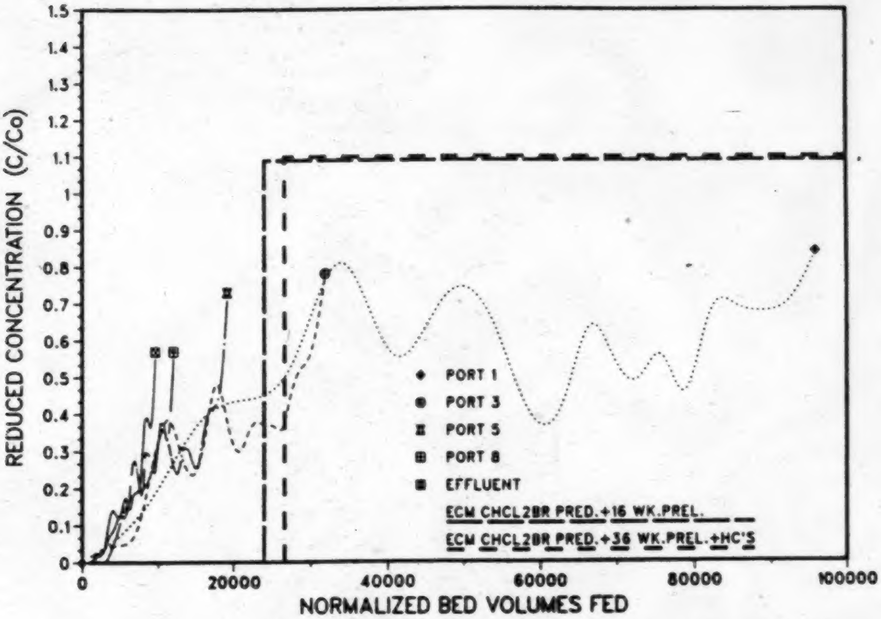


Figure IX.5 Effect of Variable Pre-Loading Time (16 and 36 Weeks) on ECM Prediction of Bromodichloromethane (1986 Ceca 830 Ported Bed)

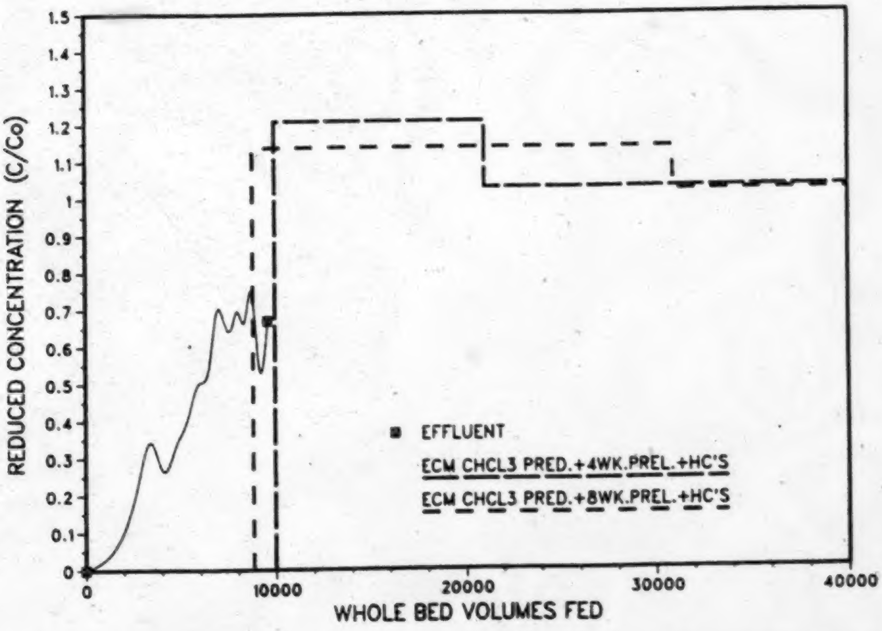


Figure IX.6 Effect of Variable Pre-Loading Time (4 and 8 Weeks) on ECM Prediction of Chloroform Breakthrough (1986 Filtrasorb 300® Bed)

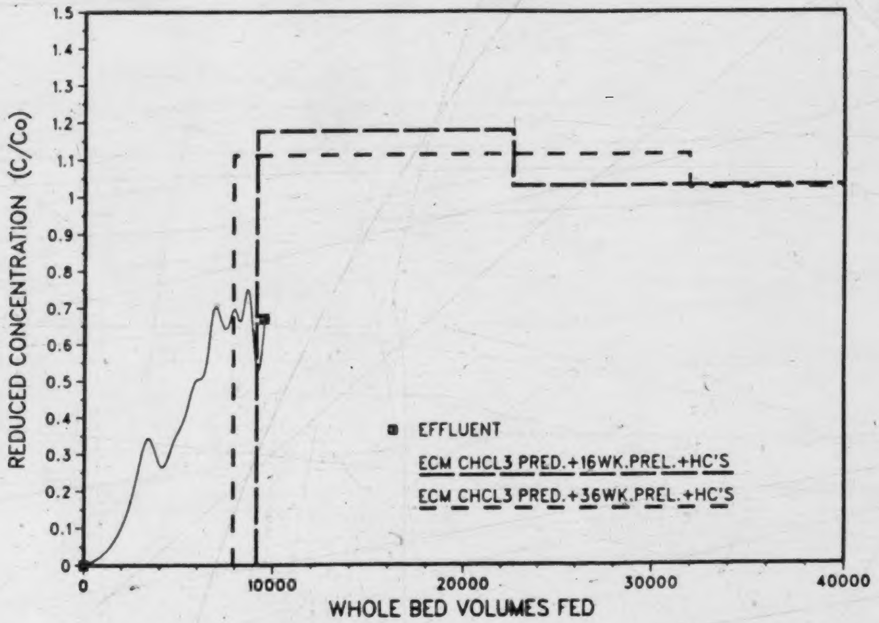


Figure IX.7 Effect of Variable Pre-Loading Time (16 and 36 Weeks) on ECM Prediction of Chloroform Breakthrough (1986 Filtrasorb 300® Bed)

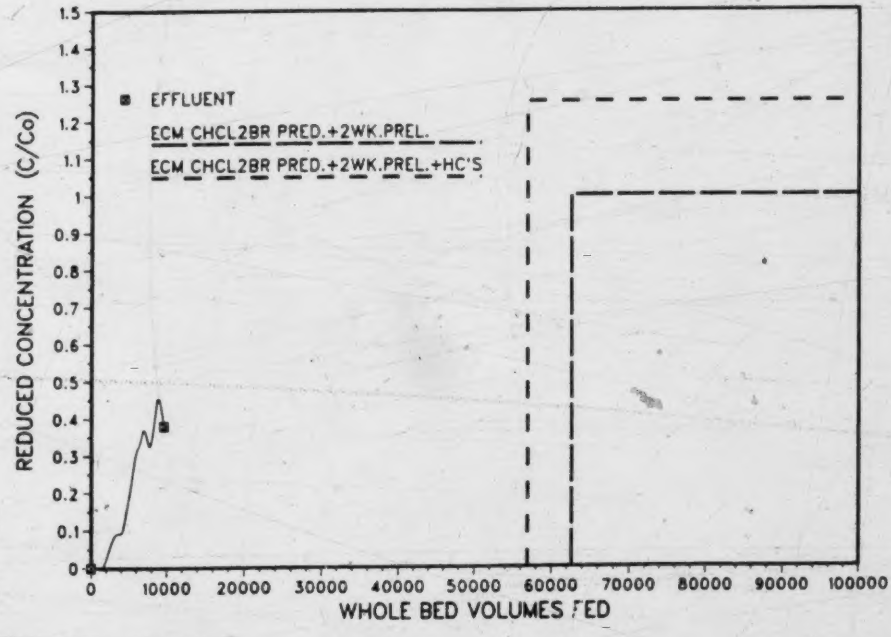


Figure IX.8 Effect of Variable Pre-Loading Time and HC's on ECM Prediction of Bromodichloromethane Breakthrough (1986 Filtrasorb 300® Bed)

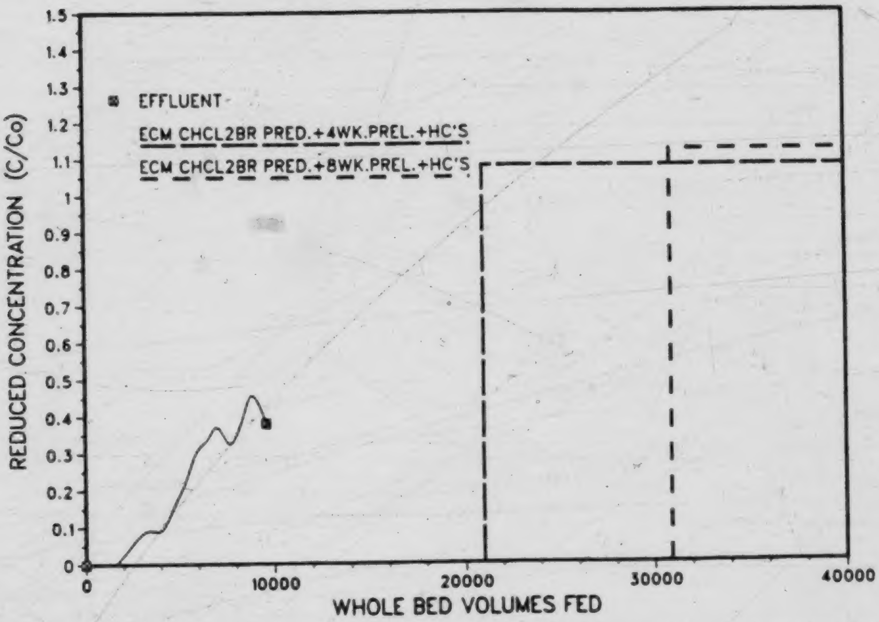


Figure IX.9 Effect of Variable Pre-Loading Time (4 and 8 Weeks) on ECM Prediction of Bromodichloromethane Breakthrough (1986 Filtrasorb 300® Bed)

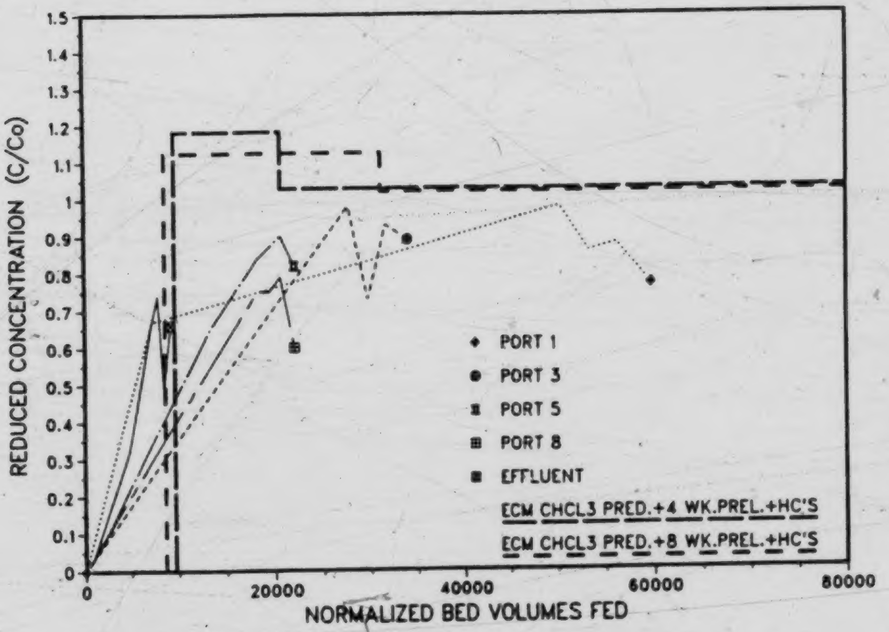


Figure IX.10 Effect of Variable Pre-Loading Time (4 and 8 Weeks) on ECM Prediction of Chloroform Breakthrough (1987 Filtrasorb 300® Ported Bed)

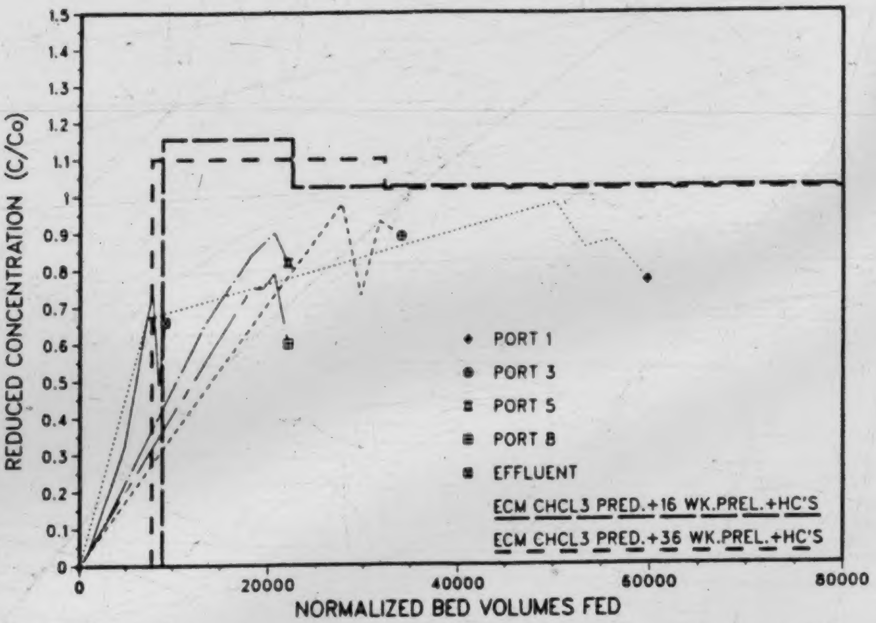


Figure IX.11 Effect of Variable Pre-Loading Time (16 and 36 Weeks) on ECM Prediction of Chloroform Breakthrough (1987 Filtrasorb 300® Ported Bed)

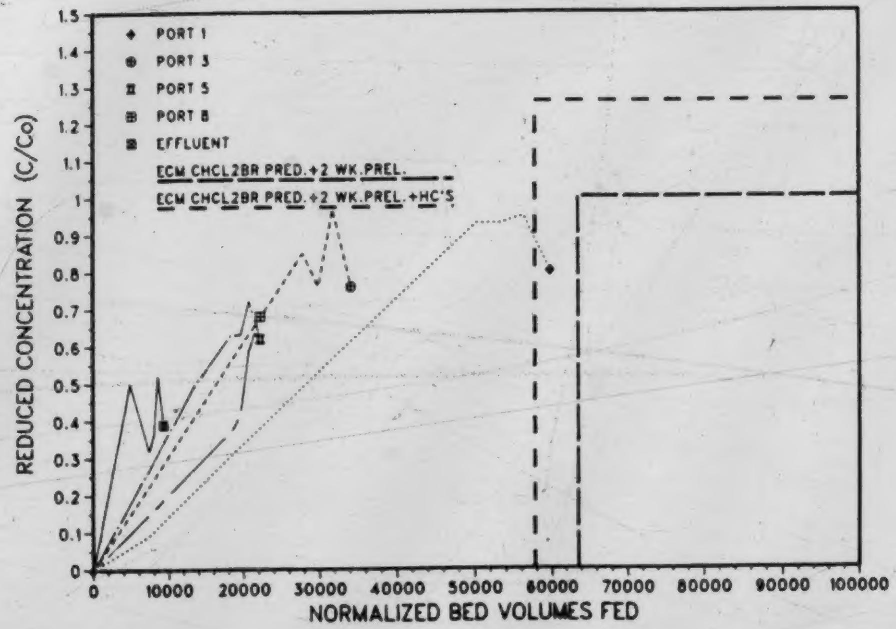


Figure IX.12 Effect of Variable Pre-Loading Time and HC's on ECM Prediction of Bromodichloromethane Breakthrough (1987 Filtrasorb 300® Ported Bed)

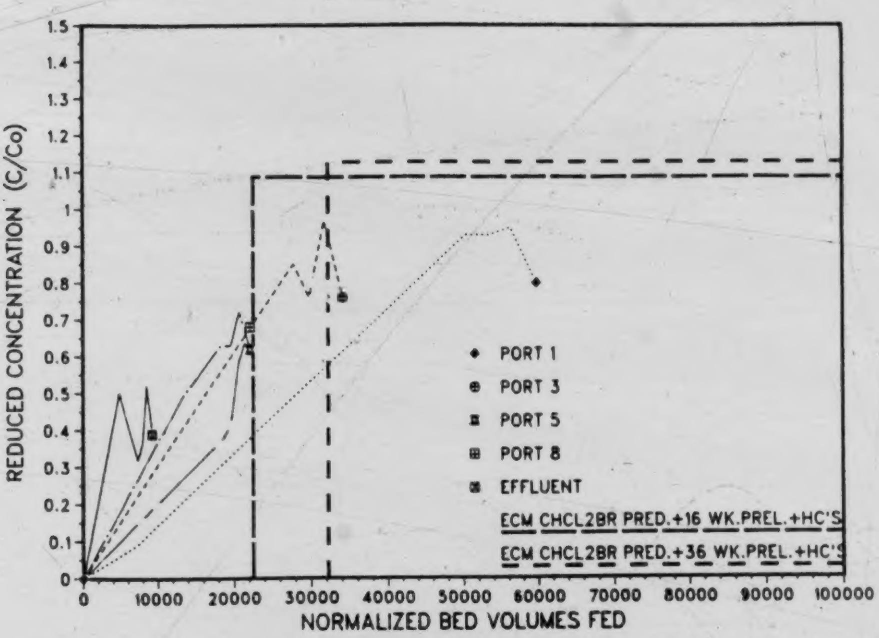


Figure IX.13 Effect of Variable Pre-Loading Time (16 and 36 Weeks) on ECM Prediction of Bromodichloromethane Breakthrough (1987 Filtrasorb 300® Ported Bed)

Appendix X

Evaluation of Synthesized MX Purity

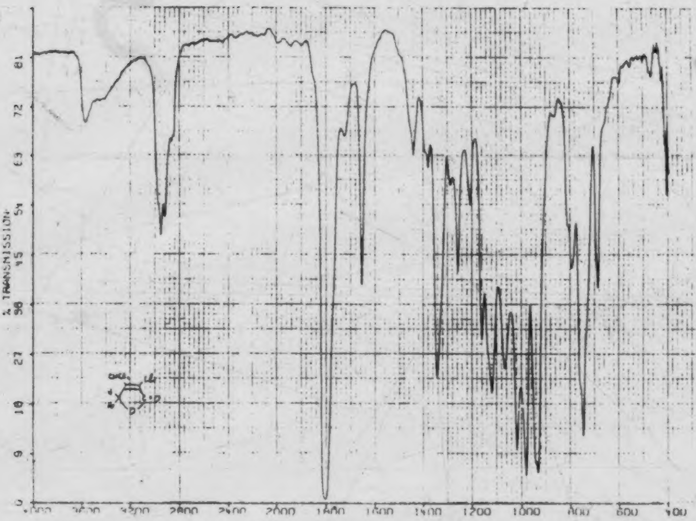


Figure X.1 IR Spectrum for Synthesized MX

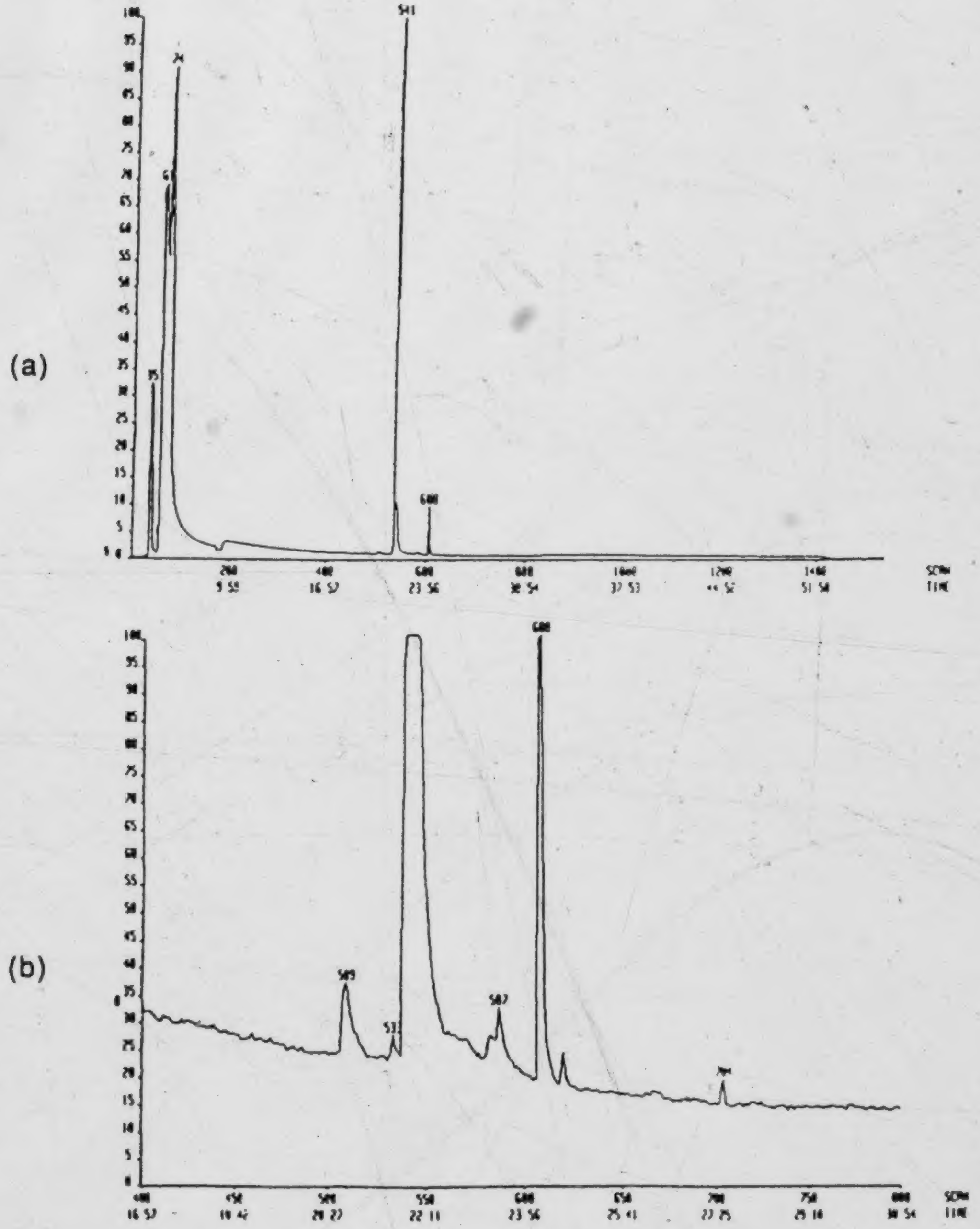


Figure X.2 Total Ion Current Chromatograms for MX. (a) Raw Chromatogram, (b) Enlargement of MX/EMX Region to Show Small Peaks

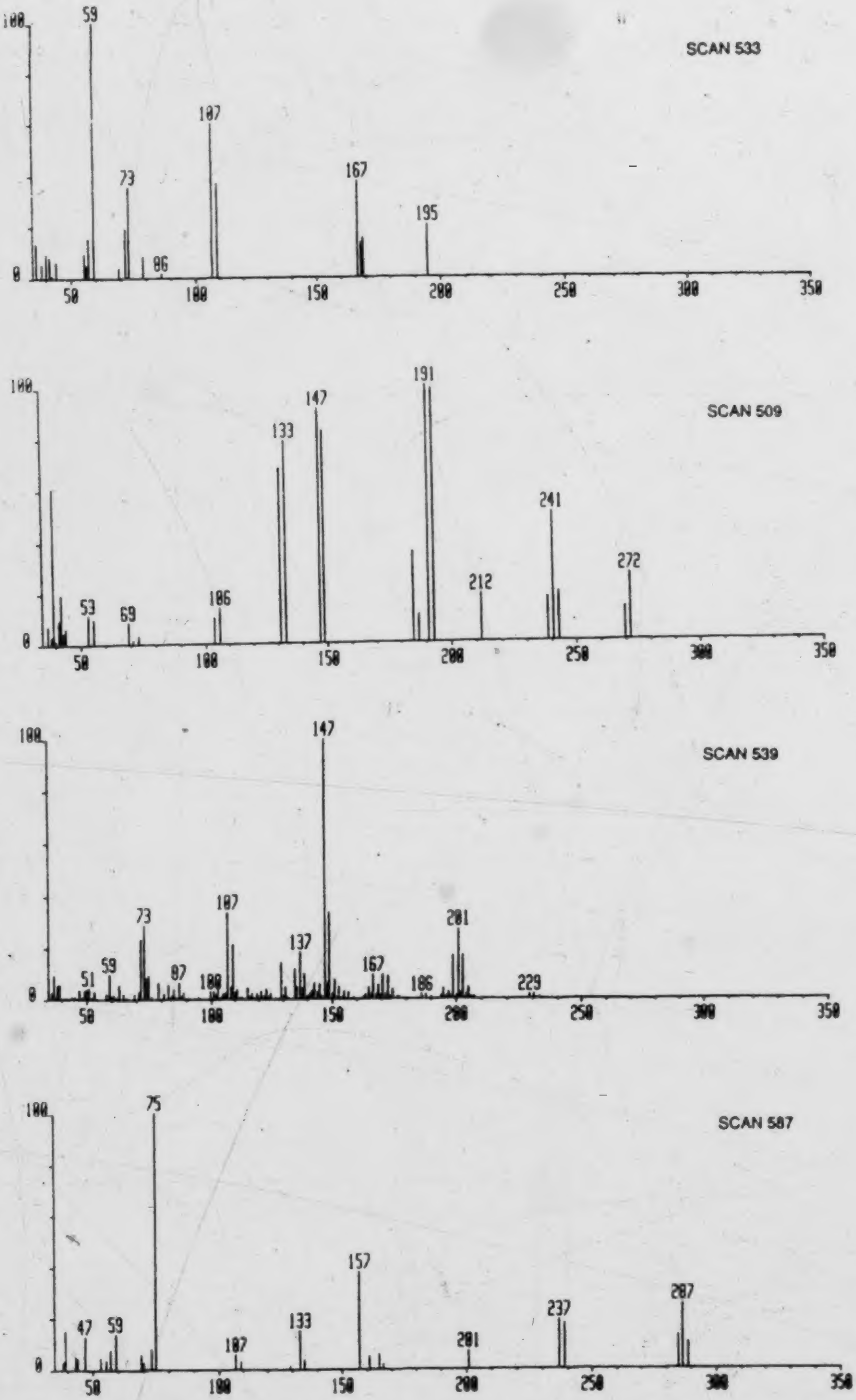


Figure X.3 Mass Spectra of Peaks Observed in MX Standard

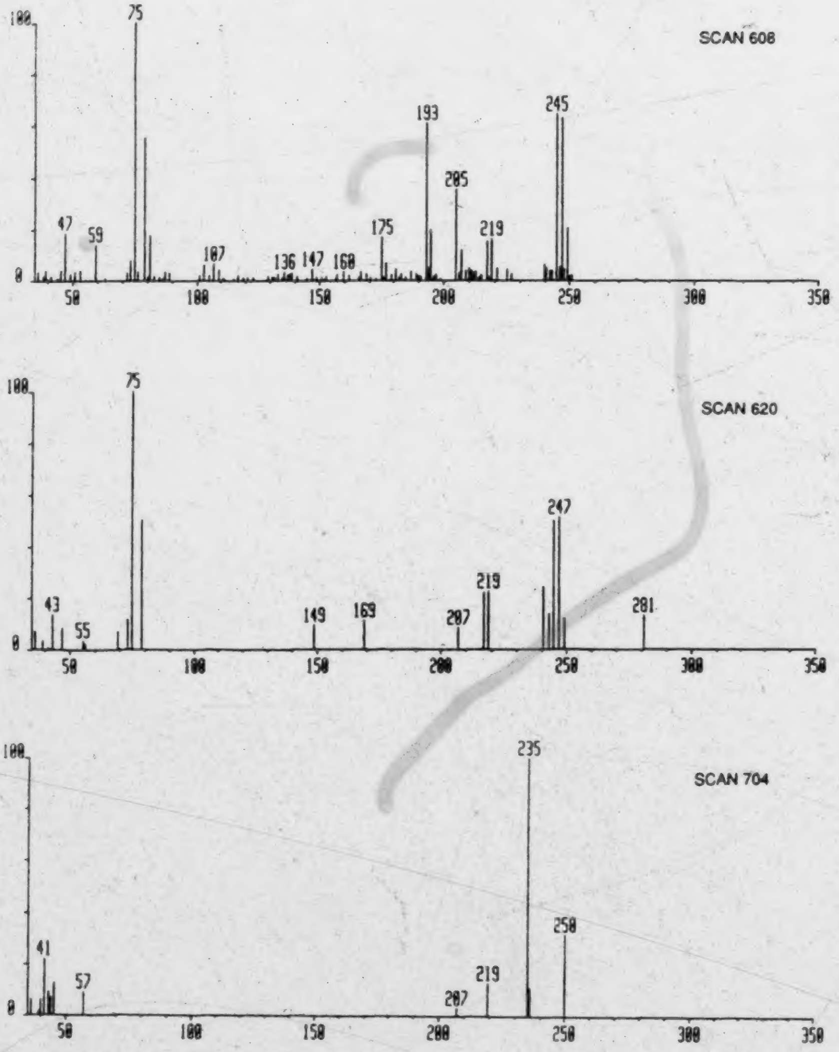


Figure X.3 Cont'd. Mass Spectra of Peaks Observed in MX Standard

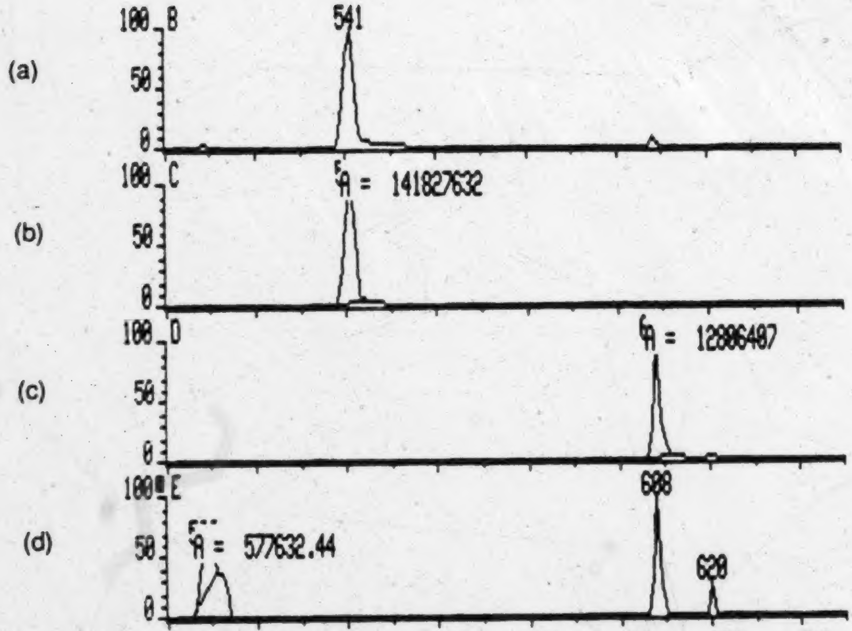


Figure X.4 (a) Total and (b) Single Ion Current Chromatograms for MX (m/e 201), (c) EMX (m/e) 245 and (d) MBA (m/e 241)

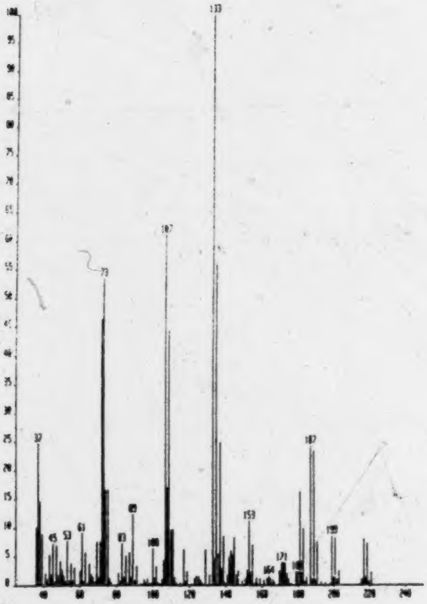


Figure X.5 Direct Probe Mass Spectrum of Underivatized MX

Appendix XI

Derivatization Investigations

The objectives of derivatization experimentation were:

i) To establish a derivatization procedure yielding the cleanest chromatography and the best reproducibility among replicate injections of a given sample.

ii) To limit formation and number of derivatization by-products which might interfere with chromatogram interpretation.

iii) To tentatively identify the origin of derivatization by-products.

1. Comparison of Sample State (Dry *vs* Solvated) on Derivatization

For these experiments three different sample preparation techniques were employed to evaluate: 1) the effect of the presence or absence of solvent prior to derivatization, and 2) any effects of different solvents on derivitization. The experimental design is shown in Figure XI.1. Samples A and B were used to compare the effect of taking the solvent (ethyl acetate) to dryness prior to derivatization. Sample A was taken to dryness under a gentle flow of nitrogen. Samples B and C were used for the solvent comparison. In these cases, the volume of solvent was reduced to approximately 100 µl.

For purposes of solvent comparison 0.5 mL of ethyl acetate and 0.5 mL of diethyl ether were measured into 1 dram vials (samples A

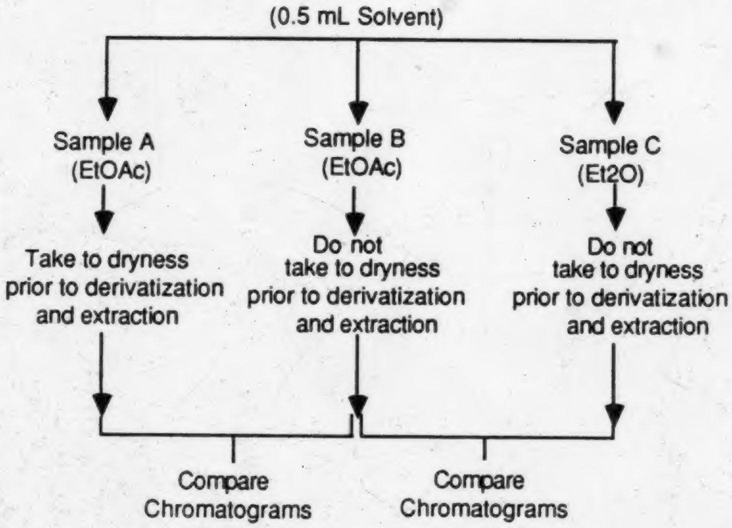

(0.5 mL Solvent)
Sample A
(EtOAc)
Sample B
(EtOAc)
Sample C
(Et2O)
Take to dryness
prior to derivatization
and extraction
Do not
take to dryness
prior to derivatization
and extraction
Do not
take to dryness
prior to derivatization
and extraction
Compare
Chromatograms
Compare
Chromatograms

Figure XI.1 Experimental Design Procedure Used to Compare Effect of Sample State and Solvent Type on Derivatization

and B). Sample C contained 0.5 mL of diethyl ether instead of ethyl acetate. 10 µL of 130.5 ng/µL mucobromic acid (MBA) and 490 ng of MX (from 2 µL of 245 ng/µL of MX) were added to each vial.

All three samples were derivatized using 0.5 mL of a 2% sulfuric acid solution in methanol. They were then heated at 70°C for 1 hour. Afterwards, they were allowed to cool to room temperature and were quenched with 1.0 mL of a 2% sodium bicarbonate solution in water. The pH was measured with pH paper to ensure that the solutions obtained were neutral. The resulting derivatives were extracted with 3x1 mL portions of hexane. The organic phases were dried using anhydrous sodium sulfate and concentrated to approximately 100 µL under a gentle flow of nitrogen. All samples were analyzed in duplicate by GC/ECD.

For ethyl acetate, taking the solvent to dryness prior to derivatization resulted in MX/MBA area ratios that in some cases were more than twice as high as similar samples not taken to dryness (Table XI.1, Sample A vs Sample B). In contrast, the EMX/MBA area ratios were much lower in the sample taken to dryness. Results presented by Kronberg et al. (1987) showed that mutagenicity did not change when XAD extracts were taken to dryness by applying a gentle stream of nitrogen. No results were stated concerning the relative concentrations of MX and EMX.

If only MX is of interest in a particular sample, evaporating extracts to dryness for derivatization appears to be desirable since it reduces peaks that may interfere with the MX peak. If EMX is also of interest taking extracts to dryness is not recommended since the concentration of any EMX present may also be reduced.

Table XI.1 Effect of Sample State on Reproducibility of Derivatization Method

Sample	Solvent	Mass MBA (μg)	Area Counts			MX/MBA Area Ratio	EMX/MBA Area Ratio
			MBA	MX	EMX		
A	Ethyl acetate (dryness)	1.305	14036000	291850	LD	0.0208	
		1.305	12161000	198220	11656	0.0163	0.0010
B	Ethyl acetate	1.305	17467000	153300	97197	0.0088	0.0056
		1.305	17709000	150070	100850	0.0085	0.0057
C	Diethyl ether	1.305	14848000	248090	8321	0.0167	0.0006
		1.305	10396000	123110	20347	0.0118	0.0020

LD-Less than detection limit

2. Investigation of Unknown Peaks From Derivatization

Figure XI.2 shows chromatograms obtained for a derivatized sample taken to dryness (Sample A) and for a sample in which a small amount of solvent remained (Sample B). There are fewer unknown peaks for the sample taken to dryness. The absence of solvent coincided with the disappearance of the EMX peak and two major peaks, representing unknown compounds, one at approximately 3.7 minutes (U1), and the other at approximately 9.9 minutes (U2). The disappearance of peak U2 is of greatest interest since it eliminated a previously noted interference with the MX peak which occurred at approximately 9.7 minutes. In addition, doubling of the solvent peak in sample B (U1) was not observed when compared to sample A which was taken to dryness.

Sample C which used diethyl ether as the solvent did not show any doubling of the solvent peak, suggesting that this phenomenon was specific to ethyl acetate (Figure XI.2). The peak U2 was not as large in the diethyl ether sample as compared to the ethyl acetate sample but did interfere with peak delineation to a small degree. Further experimentation would be required to identify all of the peaks observed in the analysis of standards and samples.

3. Reproducibility of Derivatization Method

On the basis of comparing area counts, the best reproducibility results for duplicate injections were obtained with Sample B (Table XI.2). However this sample provided the lowest MX/MBA area ratio for MX and the highest EMX/MBA area ratio. These results suggest a solvent interaction in the derivatization procedure.

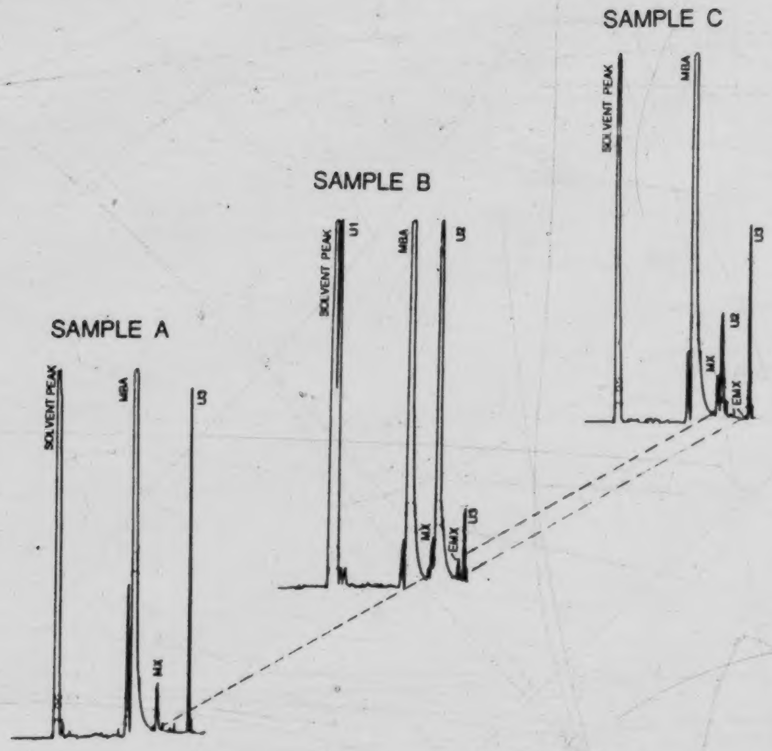


Figure XI.2 Chromatograms Obtained for Derivatization Experiment Samples A, B and C

Table XI.2 Internal Standard (MBA) Results

Sample Volume Injected(µL) Extract/Hexane	Sample	MBA Area Counts (x10EE7)	MX Area Counts (x10EE7)	MX/MBA Area Counts Ratio
2/0	C6 (Blank)			
2/0	C6 (Blank)			
2/0	C6 (Blank)			
2/0	C6 (Blank)			
1.5/1	MBA Check 1	2.49	1.21	0.484
1.5/1	MBA Check 1	2.78	1.32	0.474
1.5/1	MBA Check 1	2.20	1.04	0.474
1.5/1	MBA Check 2	2.20	1.09	0.498
1.5/1	MBA Check 2	2.63	1.22	0.466
1.5/1	MBA Check 3	4.05	2.06	0.510
1.5/1	MBA Check 3	4.74	2.43	0.513

MX/MBA Area Count Ratio: Average=0.488
Standard Deviation=0.0187 (3.8%)

4. Internal Standard (Mucobromic Acid) Reproducibility

A series of replicate analyses were conducted to determine the chromatographic precision of results obtained using mucobromic acid (MBA) as the internal standard. Three replicate samples containing 1 µL of 4.9 mg/mL MX and 5 uL MBA were prepared. Each of the final derivatized hexane extracts was reduced to a volume of approximately 100 µL prior to GC/ECD analyses. GC/ECD results are shown in Table XI.3.

The average MX/MBA area count ratio for this experiment was 0.488 with a standard deviation of 3.8%. This value represents the overall variability attributable to preparation, derivatization and GC analysis and is considered quite acceptable.

To assess the variability attributable to GC analysis alone, five replicate injections of the MBA check sample number 1 were conducted. These analyses followed approximately a one month sample storage period. All GC/ECD operating conditions were the same as described in the methods section except that a new DB-1 capillary column had been installed in the GC. The results presented in Table XI.3 show a relative standard deviation of 1.6% attributable to the GC portion of the analytical procedure. This represents approximately 40 per cent of the overall variability of the analysis for MX using the internal standard MBA.

Table XI.3 GC/ECD Reproducibility Results

Sample Volume Injected(µL) Extract/Hexane	Sample	MBA Area Counts (x10EE7)	MX Area Counts (x10EE7)	MX/MBA Area Counts Ratio
1.5/1	MBA Check 1	3.94	2.41	0.612
1.5/1	MBA Check 1	4.25	2.62	0.617
1.5/1	MBA Check 1	4.05	2.49	0.615
1.5/1	MBA Check 1	4.11	2.44	0.593
1.5/1	MBA Check 1	4.30	2.63	0.611

MX/MBA Area Counts Ratio: Average=0.610
Standard Deviation=0.00973 (1.6%)

Appendix XII

Individual Water Treatment Results

Table XII.1 MX/EMX Water Treatment Plant Survey Results-Plant A; Sampled December 21, 1988

	Sample Source	
Parameter	Pre-Clorinated Raw Water (As Received)	Post-Chlorinated Finished Water (As Received)
Temperature (°C) (a)	4.6	4.6
pH	8.06	7.7
Chlorine Free (mg/L) Total (mg/L)	NA 0.38	
NPTOC (mg/L)	4.86	NA
TOX (µg/L)	NA	NA
MX (ng/L) EMX (ng/L)	60.2 LD	NA NA

(a) Measured at time of sample collection
Volume of water extracted: Pre-chlorinated: 17.0L
NA-Sample not analyzed
LD-Less than detection limit

Table XII.2 MX/EMX Water Treatment Plant Survey Results-Plant A; Sampled January 24, 1989

	Sample Source	
Parameter	Pre-Clorinated Raw Water (As Received)	Post-Chlorinated Finished Water (As Received)
Temperature (°C) (a)	4.5	4.5
pH	7.62	7.32
Chlorine Free (mg/L) Total (mg/L)	NA 0.91	NA 0.97
NPTOC (mg/L)	4.24	3.53
TOX (µg/L)	428	
MX (ng/L) EMX (ng/L)	LD 210	LD 648

(a) Measured at time of sample collection
Volume of water extracted: Pre-chlorinated: 19.5L, Post-chlorinated: 19.5L
NA-Sample not analyzed
LD-Less than detection limit

Table XII.3 MX/EMX Water Treatment Plant Survey Results-Plant B; Sampled December 13, 1988 (16:00 hr)

Parameter	Sample Source	
	Raw Water (As Received)	Raw Water (Following MX spike)
Temperature (°C) (a)	6	NA
pH	7.66	NA
NPTOC (mg/L)	1.76	NA
MX (ng/L)	LD	LD
EMX (ng/L)	LD	LD

Volume of water extracted: Raw 4L, MX spiked 4L
NA-Sample not analyzed
LD-Less than detection limit
(a) Measured at time of sample collection

Table XII.4 MX/EMX Water Treatment Plant Survey Results-Plant B; Sampled December 16, 1988 (9:30 hr)

Parameter	Sample Source		
	Raw Water (As Received)	Raw Water (Following Lab Chlorination)(a)	Raw Water (Following Reaction Time)(b)
Temperature (°C) (c)	7	NA	NA
pH	7.86	NA	NA
Chlorine			
Free (mg/L)	NA	NA	NA
Total (mg/L)	NA	2.63	2.15
NPTOC (mg/L)	2.67	NA	NA
MX (ng/L)	5.71	NA	LD
EMX (ng/L)	LD	NA	11.6

Volume of water extracted: Raw: 9.55L, Lab. Chlorinated: 9.50L.
(a) Chlorine added (mg/L): 1.69 mL of 15,599 mg/L of NaOCl
(b) Reaction time (Hr.): 64.5
(c) Measured at time of sample collection

NA-Sample not analyzed
LD-Less than detection limit

Table XII.5 MX/EMX Water Treatment Plant Survey Results-Plant C; Sampled January 9, 1989 (14:00 hr)

	Sample Source	
Parameter	Pre-Clorinated Raw Water (As Received)	Post-Chlorinated Finished Water (As Received)
Temperature (°C) (a)	4.6	4.6
pH	7.66	6.97
Chlorine Free (mg/L) Combined (mg/L) Total (mg/L)	 NA NA 0.24	 NA NA 4.3
NPTOC (mg/L)	15.94	4.32
TOX (µg/L)	352	607
MX (ng/L) EMX (ng/L)	83.3 LD	LD LD

(a) Measured at time of sample collection
Volume of water extracted: Pre-chlorinated: 18L, Post-chlorinated: 18L
NA-Sample not analyzed

Table XII.6 MX/EMX Water Treatment Plant Survey Results-Plant C; Sampled January 23, 1989 (12:00 hr)

	Sample Source	
Parameter	Pre-Clorinated Raw Water (As Received)	Pre-Chlorinated Raw Water (Spiked with MX)
Temperature (°C) (a)	3.8	3.8
pH	7.35	7.00
Chlorine Free (mg/L) Combined (mg/L) Total (mg/L)	 NA NA 0.96	 NA NA 0.53
NPTOC (mg/L)	13.49	13.84
TOX (µg/L)	217	NA
MX (ng/L) EMX (ng/L)	37.8 311	1178 57.2

(a) Measured at time of collection
(b) Samples chlorinated @ WTP
(c) Cultures used for analysis died during experiment
Volume of water extracted: Pre-chlorinated: 18L, Post-chlorinated: 18L
NA-Sample not analyzed
LD-Less than detection limit
AOC Post-filtered sample: 45 µg/L

Table XII.7 MX/EMX Water Treatment Plant Survey Results-Plant D; Sampled January 12, 1989 (11:30 hr)

Parameter	Sample Source			
	Raw Water (As Received)	Raw Water (Following Lab Chlorination)(a)	Raw Water (Following Reaction Time)(b)	Post-Chlorinated Finished Water (As Received)
Temperature (°C) (c)	3	NA	NA	3
pH	7.98	NA	NA	8.11
Chlorine				
Free (mg/l)	NA	21.0	1.21	0.47
Combined (mg/L)	NA	3.72	1.12	0.42
Total (mg/L)	LD	25.9	2.86	1.31
NPTOC (mg/L)	16.97	NA	NA	20.91
TOX (µg/L)	60	NA	3184	754
MX (ng/L)	NA	NA	LD	LD
EMX (ng/L)	NA	NA	LD	LD

Volume of water extracted: Raw 16.8L, Finished 18L.
(a) Chlorine added (mg/L): 19.6mL of 15,599 mg/L of NaOCl
(b) Reaction time (Hr.): 65 hrs
(c) Measured at time of collection

NA-Sample not analyzed
LD-Less than detection limit

Table XII.8 MX/EMX Water Treatment Plant Survey Results-Plant E; Sampled January 16, 1989 (11:50 hr)

Parameter	Sample Source			
	Raw Water (As Received)	Raw Water (Following Lab Chlorination)(a)	Raw Water (Following Reaction Time)(b)	Post-Chloraminated Finished Water (As Received)
Temperature (°C) (c)	4.1	NA	NA	4.6
pH	7.61	NA	NA	7.52
Chlorine				
Free (mg/L)	NA	28.6	5.5	0.66
Combined (mg/L)	NA	1.33	1.8 (d)	0.98
Total (mg/L)	0.26	27.5	16.4	NA
NPTOC (mg/L)	27.10	NA	NA	5.41
TOX (µg/L)	146	NA	3752	245
MX (ng/L)	NA	NA	LD	LD
EMX (ng/L)	NA	NA	LD	LD

Volume of water extracted: Raw 16.58L, Finished 18L
(a) Chlorine added (mg/L): 30.6 mL of 15,599 mg/L of NaOCl
(b) Reaction time (Hr.): 41.5
(c) Measured at time of collection
(d) Some chlorine may have been lost due to strong gas production upon acidification
(e) Post-filter (AOC): 130 µg/L

NA-Sample not analyzed
LD-Less than detection limit

Table XII.9 MX/EMX Water Treatment Plant Survey Results-Plant F; Sampled January 19, 1989 (11:30 hr)

Parameter	Sample Source			
	Raw Water (As Received)	Raw Water (Following Lab Chlorination)(a)	Raw Water (Following Reaction Time)(b)	Post-Chlorinated Finished Water (As Received)
Temperature (°C) (c)	4	NA	NA	4
pH	7.64	NA	NA	7.58
Chlorine				
Free (mg/L)	NA	19.9	2.75	1.12
Combined (mg/L)NA		2.49	3.72	0.85
Total (mg/L)	LD	29.9	8.42	2.39
NPTOC (mg/L)	24.12	NA	NA	8.20
TOX (µg/L)	307	NA	3363	1010
MX (ng/L)	NA	NA	59.83	27
EMX (ng/L)	NA	NA	0.81	38.9

Volume of water extracted: Raw 17L, Finished 18L.
(a) Chlorine added (mg/L): 27.4 mL of 15,590 mg/L of NaOCl
(b) Reaction time (Hr.): 40.5
(c) Measured at time of sample collection

NA-Sample not analyzed
LD-Less than detection limit

Appendix XIII

GC/MS Analyses of GAC Extracts

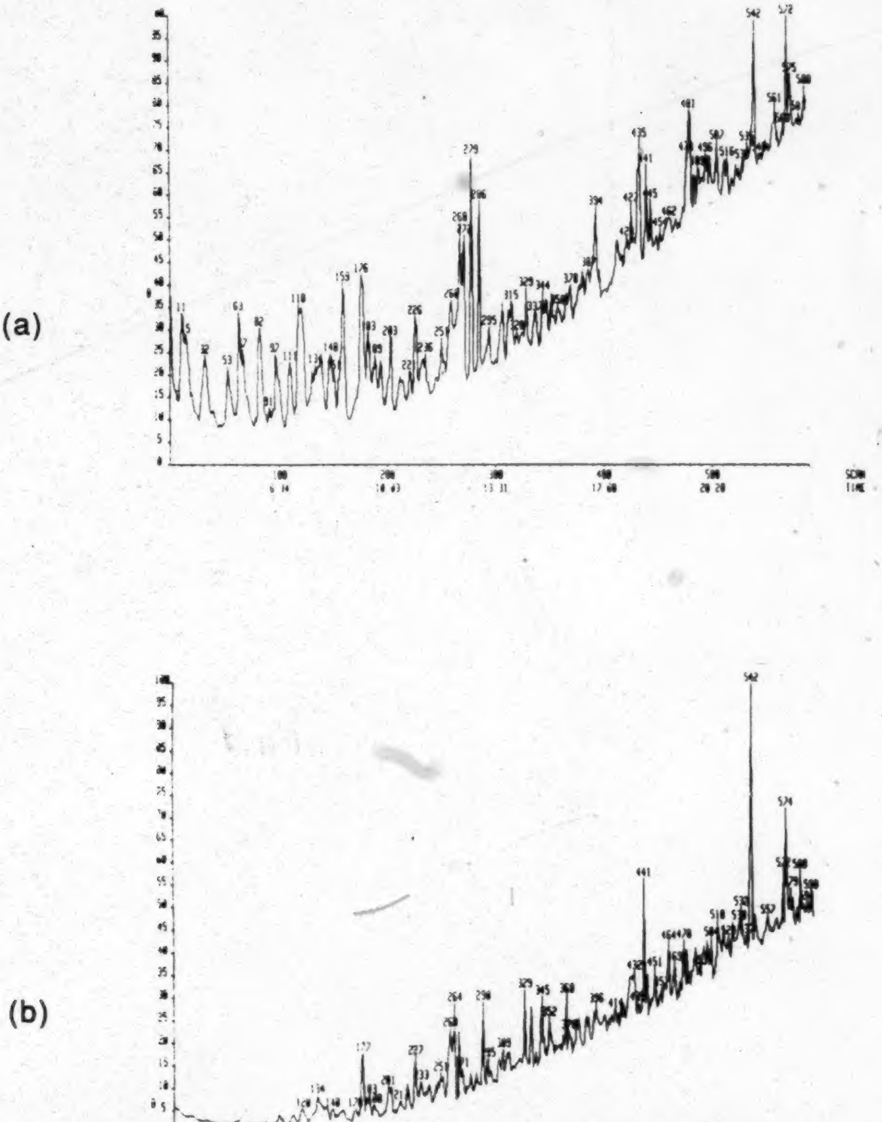


Figure XIII.1 Total Ion Current Chromatogram for Soxhlet Extracts of GAC from (a) Plant A and (b) Plant B

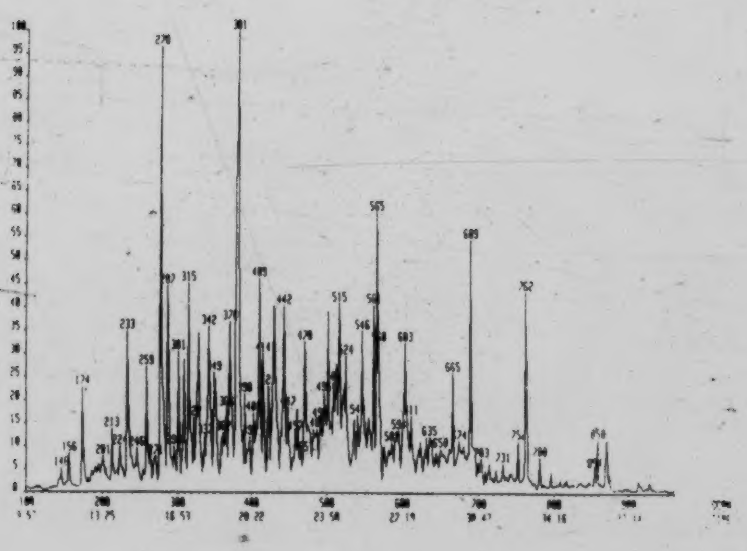


Figure XIII.2 Total Ion Current Chromatogram for Soxhlet Extracted Plant A Pilot Column GAC

Appendix XIV

Isotherm Data Collected at pH 6, 7 and 8

Table XIV.1 GC/ECD Data for MX Sample Blanks, pH 6

Experiment No. : EXP-MX.VI.3-89

19 L of Milli-Q water buffered at pH 6 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

Sample	Run No.	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio	MX (MBA;µg/L)	MX Average (MBA;µg/L)	MX (TCT;µg/L)	MX Average (TCT;µg/L)
B1 (a)	477	225830	3213900	247480	14.2315	12.9865	1004.0		76.2245	
•	548	1166800	9277300	466030	7.9511	19.9071	291.7	647.9	116.9383	96.5814
B2	478	948630	8199200	443760	8.6432	18.4767	349.3		108.5231	
•	549	3174800	17293000	714160	5.4470	24.2145	126.9	238.1	142.2786	125.4009
B3	479	561000	2395100	356560	4.2693	6.7172	72.8		39.3425	
•	550	1898900	5541100	541390	2.9181	10.2350	29.3	51.0	60.0372	49.6898
B4	480	278380	3961000	218810	14.2288	18.1025	1003.6		106.3217	
•	551	1360900	10523000	455950	7.7324	23.0793	274.6	639.1	135.6004	120.9611
B5	481	395320	5724000	282890	14.4794	20.2340	1040.8		118.8616	
•	552	1312200	11510000	444380	8.7715	25.9013	360.5	700.7	152.2020	135.5318
B6	482	1528	370160	13114	242.2513	28.2263	316134.9		165.8804	
•	520	3642	973570	15756	267.3174	61.7904	385126.3		363.3380	
•	553	14720	1299200	15313	88.2609	84.8429	41590.2	247617.2	498.9560	342.7248

(a) Sample spilled while drying over sodium sulfate

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.2 GC/ECD Data for MX Isotherm, pH 6

EXPERIMENT No. : EXP-89.MX.VI-3

19 L of Milli-Q water buffered at pH 6 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

SAMPLE	RUN NO.	CARBON (mg)	MBA AREA COUNTS	MX AREA COUNTS	TCT AREA COUNTS	MX/MBA AREA RATIO	MX/TCT AREA RATIO	MX (MBA;µg/L)	MX Average (MBA;µg/L)	MX (TCT;µg/L)	MX Average (TCT;µg/L)
1	483	2.23	944880	2511100	1589500	2.6576	1.5798	24.6733		9.8981	
•	534	2.23	1466500	2156300	2150300	1.4704	1.0028	4.8904	14.7819	6.2829	8.0905
2	484	3.19	870110	141940	2515500	0.1631	0.0564	1.9112		0.3535	
•	535	3.19	1311900	199970	3345400	0.1524	0.0598	1.9681	1.9397	0.3745	0.3640
3	485	4.70	14563000	895440	5765600	0.0615	0.1553	2.5053		0.9731	
•	536	4.70	19533000	1279400	6560500	0.0655	0.1950	2.4798	2.4925	1.2218	1.0975
4	486	5.95	6664400	628580	3943900	0.0943	0.1594	2.3004		0.9985	
•	537	5.95	13878000	1511300	7386600	0.1089	0.2046	2.2134	2.2569	1.2819	1.1402
5	487	6.98	4361700	86344	2015500	0.0198	0.0428	2.7835		0.2684	
•	538	6.98	5805200	140810	2459400	0.0243	0.0573	2.7528	2.7681	0.3587	0.3136
6	493	8.35	26809	70430	333940	2.6271	0.2109	23.9620		1.3214	
•	539	8.35	39691	134110	8425100	3.3789	0.0159	44.6297	34.2958	0.0997	0.7106
7	489	9.89	8074500	104460	8425100	0.0129	0.0124	2.8312		0.0777	
•	516	9.89	7117700	98507	8647400	0.0138	0.0114	2.8249		0.0714	
•	517	9.89	9356100	144570	9280500	0.0155	0.0156	2.8136		0.0976	
•	540	9.89	3055500	52920	2613300	0.0173	0.0203	2.8006		0.1269	
•	541	9.89	17682000	382520	12926000	0.0216	0.0296	2.7708	2.8082	0.1854	0.1118
8	518	11.36	3432500	47323	4578800	0.0138	0.0103	2.8252		0.0648	
•	542	11.36	11692000	178690	9878200	0.0153	0.0181	2.8146		0.1133	
•	543	11.36	3573700	43371	3224600	0.0121	0.0135	2.8368	2.8256	0.0843	0.0875
9	491	13.60	1554900	25542	1831000	0.0164	0.0139	2.8068		0.0874	
•	519	13.60	3012200	61696	2463900	0.0205	0.0250	2.7787		0.1569	
•	546	13.60	3590300	81665	2790800	0.0227	0.0293	2.7631	2.7829	0.1833	0.1425
10	492	15.80	5420400	48410	4316500	0.0089	0.0112	2.8593		0.0703	
•	547	15.80	9376000	114610	6185300	0.0122	0.0185	2.8361	2.8477	0.1161	0.0932

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.3 GC/ECD Data for MX Standard Curve (for pH 6 Isotherm)

ExperimentNo.: EXP-89.MX.VI-3

Sample	Run No.	MX Conc. (µg/µL)	MX Vol. (µL)	MX Std. (µg)	EMX Std. (µg)	MX/MBA Mass Ratio	EMX/MBA Mass Ratio	MX/TCT Mass Ratio	EMX/TCT Mass Ratio	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio
MBA+TCT Blank	523	-	-	-	-	-	-	-	-	15373		12745	-	-
"	566	-	-	-	-	-	-	-	-	22521		13993	-	-
"	567	-	-	-	-	-	-	-	-	20789		12598	-	-
STD 66.512 ng	524	0.033256	2.0	0.0641	0.0025	0.0402	0.0015	21.4	0.8	6020300	63852	2303200	0.0106	0.0277
"	558	0.033256	2.0	0.0641	0.0025	0.0402	0.0015	21.4	0.8	5617300	62144	2191800	0.0111	0.0284
STD 332.56 ng	525	0.033256	10.0	0.3203	0.0123	0.2008	0.0077	106.8	4.1	9238	2873	67724	0.3110	0.0424
STD 997.68 ng	526	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	7999500	863730	5077100	0.1080	0.1701
"	559	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	8052100	880220	5257200	0.1093	0.1674
STD 1995.36 ng	527	0.33256	6.0	1.9215	0.0738	1.2047	0.0463	640.5	24.6	1055600	376580	804220	0.3567	0.4683
"	560	0.33256	6.0	1.9215	0.0738	1.2047	0.0463	640.5	24.6	1409700	502130	905830	0.3562	0.5543
STD 9976.8 ng	528	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	3014300	3614500	2750800	1.1991	1.3140
"	561	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	2136000	2849300	1854700	1.3339	1.5363
STD 49884 ng	529	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	4401700	18110000	2157000	4.1143	8.3959
"	562	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	6679100	25381000	2972400	3.8001	8.5389
STD 99768 ng (a)	531	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	9631400	45209000	2832400	4.6939	15.9614
"	563	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	11474000	51608000	3128000	4.4978	16.4987

(a) Not included in calibration since MX area counts appear much larger than expected; could be reaching detector oveload

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

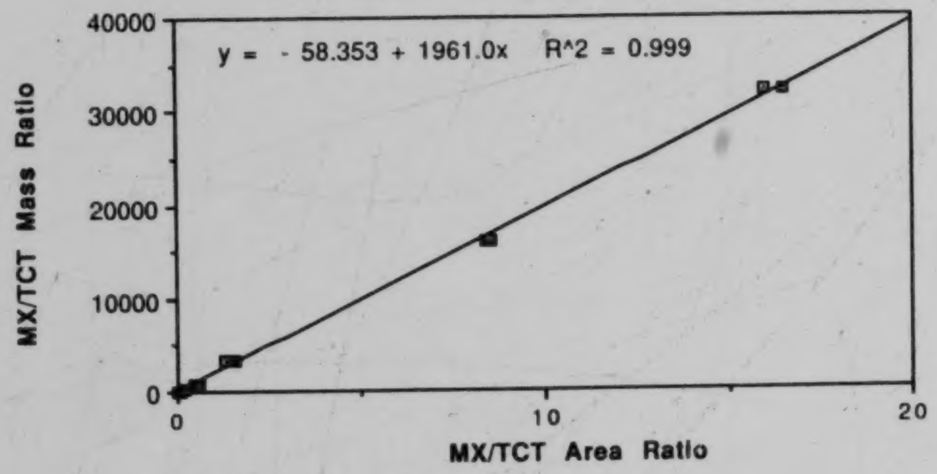


Figure XIV.1 MX Calibration Using TCT Internal Standard (for pH 6 Isotherm)

Table XIV.4 GC/ECD Data for MX Sample Blanks, pH 7

EXPERIMENT No. : EXP-89.MX.VI-4

19 L of Milli-Q water buffered at pH 7 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

SAMPLE	RUN NO.	MBA AREA COUNTS	MX AREA COUNTS	TCT AREA COUNTS	MX/MBA AREA RATIO	MX/TCT AREA RATIO	MX (MBA;µg/L)	MX Average (MBA;µg/L)	MX (TCT;µg/L)	MX Average (TCT;µg/L)
B1	575	5094000	33411000	1492200	6.5589	22.3904	99.2		86.9	
"	656	4926000	29987000	1428600	6.0875	20.9905	91.9	95.5	81.5	84.2
B2	576	3535800	19079000	737900	5.3959	25.8558	81.2		100.2	
"	657	3990700	20507000	737900	5.1387	27.7910	77.2	79.2	107.7	103.9
B3	577	3329500	18364000	654840	5.5155	28.0435	83.0		108.6	
"	658	3280100	17912000	665140	5.4608	26.9297	82.2	82.6	104.4	106.5
B4	578	2158200	19241000	434650	8.9153	44.2678	135.6		171.1	
"	659	1360900	10523000	455950	7.7324	23.0793	117.3	126.4	89.5	130.3
B5	579	958050	19260000	47291	20.1242	407.6886	308.8		1570.0	
"	660	876510	17918000	45910	20.4424	390.2853	313.7	311.3	1503.0	1536.5
B6	580	5186000	28023000	1114000	5.4036	25.1553	81.3		97.5	
"	661	4836300	25304000	1008300	5.2321	25.0957	78.6	80.0	97.3	97.4

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.5 GC/ECD Data for MX Isotherm, pH 7

Experiment No.: EXP-89.MX.VI-4

19 L of Milli-Q water buffered at pH 7 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

SAMPLE	RUN NO.	CARBON (mg)	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio	MX (MBA;µg/L)	MX Average (MBA;µg/L)	MX (TCT;µg/L)	MX Average (TCT;µg/L)
1	564	2.25	3081500	8776400	1742200	2.8481	5.0375	46.8786	45.3955	20.6635	19.8927
•	662	2.25	3499600	9336500	2008800	2.6679	4.6478	43.9123		19.1218	
2	565	3.69	7858600	4019400	2064000	0.5115	1.9474	8.4185	8.3722	8.4397	8.4605
•	663	3.69	7829500	3960400	2022800	0.5058	1.9579	8.3258		8.4812	
3	566	4.54	20806000	7530300	7596400	0.3619	0.9913	5.9572	5.9434	4.6577	4.6433
•	664	4.54	19910000	7172500	7289100	0.3602	0.9840	5.9295		4.6288	
4	567	5.79	19409000	8625200	573790	0.4444	15.0320	7.3145	7.1844	60.1988	46.1050
•	665	5.79	30216000	13218000	1168700	0.4375	11.3100	7.2003		45.4757	
•	667	5.79	31337000	13648000	1173700	0.4355	11.6282	7.1686		46.7343	
5	568	7.08	80311000	545340	3403300	0.0068	0.1602	0.1118	0.6006	1.3702	1.3409
•	666	7.08	8650000	572540	3938000	0.0662	0.1454	1.0895		1.3115	
6	569	8.46	7630600	930420	4027700	0.1219	0.2310	2.0070	1.9974	1.6502	1.6504
•	668	8.46	9309000	1124300	4864800	0.1208	0.2311	1.9879		1.6506	
7	570	10.07	9832100	765540	1771200	0.0779	0.4322	1.2816	1.2629	2.4461	2.3918
•	669	10.07	8014900	605870	1496900	0.0756	0.4047	1.2442		2.3375	
8	571	11.33	10540000	913040	3760900	0.0866	0.2428	1.4258	1.3522	1.6967	1.6207
•	670	11.33	10483000	814280	3985400	0.0777	0.2043	1.2785		1.5446	
9	572	13.61	17242000	1926200	6028600	0.1117	0.3195	1.8388	1.5587	2.0003	1.7724
•	671	13.61	10483000	814280	3985400	0.0777	0.2043	1.2785		1.5446	
10	574	16.25	8234100	450730	2014900	0.0547	0.2237	0.9010	0.8827	1.6213	1.5877
•	672	16.25	8103500	425550	2058500	0.0525	0.2067	0.8644		1.5541	

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.6 GC/ECD Data for MX Standard Curve (for pH 7 Isotherm)

Experiment No.: EXP-90.MX.VI-4

Sample	Run No.	MX Conc. (µg/µL)	MX Vol. (µL)	MX Std. (µg)	EMX Std. (µg)	MX/MBA Mass Ratio	EMX/MBA Mass Ratio	MX/TCT Mass Ratio	EMX/TCT Mass Ratio	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio
STD 66.512 ng	586	0.033256	2.0	0.0641	0.0025	0.0402	0.0016	21.4	0.8	3148100	31110	1940000	0.0099	0.0160
"	579	0.033256	2.0	0.0641	0.0025	0.0402	0.0016	21.4	0.8	3122300	30799	2111400	0.0099	0.0146
STD 332.56 ng	587	0.033256	10.0	0.3203	0.0123	0.2006	0.0077	106.8	4.1	19937000	843680	5834700	0.0423	0.1446
"	575	0.033256	10.0	0.3203	0.0123	0.2006	0.0077	106.8	4.1	16590000	694250	4930000	0.0418	0.1408
STD 997.68 ng	582	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	263790	113200	884010	0.4291	0.1288
"	589	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	170920	67578	954530	0.3954	0.0708
"	578	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	259670	107900	1013400	0.4156	0.1066
STD 1995.36 ng	580	0.33256	6.0	1.9215	0.0738	1.2047	0.0463	640.5	24.6	275600	129770	736530	0.4709	0.1762
"	601	0.33256	6.0	1.9215	0.0738	1.2047	0.0463	640.5	24.6	283150	140940	760960	0.4978	0.1852
STD 9976.8 ng	591	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	12996000	7262700	3538100	0.5588	2.0527
"	592	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	12702000	7178100	3370300	0.5650	2.1298
STD 49884 ng	583	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	6291600	20202000	1637200	3.2109	12.3394
"	593	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	6048000	19629000	1591100	3.2456	12.3367
STD 99768 ng	581	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	595840	7840	1269200	0.0132	0.0062
"	594	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	84943	4606	277550	0.0542	0.0166
"	595	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	69792	1551	259420	0.0222	0.0060

MBA Conc. = 0.1596 µg/µL
MBA Mass = 1.596 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

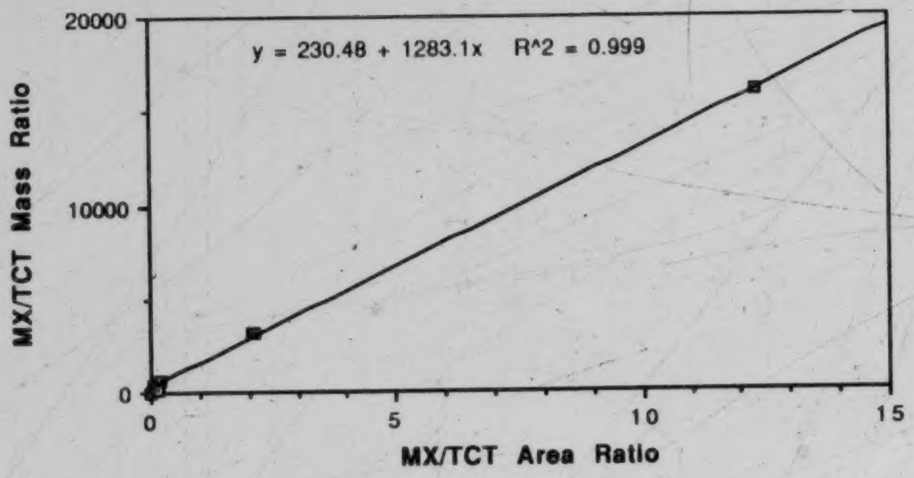


Figure XIV.2 MX Calibration Using TCT Internal Standard (for pH 7 Isotherm)

Table XIV.7 GC/ECD Data for MX Sample Blanks, pH 8

EXPERIMENT No. : EXP-89.MX.VI-5

19 L of Milli-Q water buffered at pH 8 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

SAMPLE	RUN NO.	MBA AREA COUNTS	MX AREA COUNTS	TCT AREA COUNTS	MX/MBA AREA RATIO	MX/TCT AREA RATIO	MX (MBA)(µg)	MX Average (MBA)(µg)	MX (TCT)(µg)	MX Average (TCT)(µg)
B1	596	2704400	24241000	463080	8.9635	52.3473	112.4		171.3	
"	624	2642100	23862000	444870	9.0315	53.6381	113.3	112.9	175.6	173.4603
B2	597	2161700	20940000	409810	9.6868	51.0968	121.6		167.2	
"	625	1948000	19248000	371290	9.8809	51.8409	124.1	122.9	169.7	168.4571
B3	598	2157700	19339000	396950	8.9628	48.7190	112.4		159.4	
"	626	2010000	18458000	360500	9.1831	51.2011	115.2	113.8	167.6	163.5034
B4 (a)	599	882250	14125000	152340	16.0102	92.7202	202.2		303.9	
"	627	1081100	15882000	35373	14.6906	448.9865	185.4	193.8	1473.6	888.7403
B5	600	1846600	20430000	324430	11.0636	62.9720	139.2		206.2	
"	628	2006700	20888000	369430	10.4091	56.5412	130.9	135.0	185.1	195.6673
B6	601	712740	12393000	99793	17.3878	124.1871	219.8		407.2	
"	629	918150	14124000	144110	15.3831	98.0085	194.2	207.0	321.3	364.2307

(a) Sample appeared to be contaminated (blue colour)

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.8 GC/ECD Data for MX Isotherm, pH 8

Experiment No.: EXP-89.MX.VI-5

19 L of Milli-Q water buffered at pH 8 spiked with 60 µL of 33.256 mg/mL MX diluted solution from December 9,1988 stock solution.

SAMPLE	RUN NO.	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio	MX (MBA) µg	MX Average (MBA) µg	MX (TCT) µg	MX Average (TCT) µg
1 "	602 631	2657800 2240000	20261000 18612000	1417300 1306600	7.6232 8.3089	14.2955 14.2446	103.4785 112.7863	108.1324	49.4261 49.2482	49.3372
2 "	603 632	9237100 9328500	14229000 14370000	2277000 2413200	1.5404 1.5404	6.2490 5.9547	20.9098 20.9101	20.9100	21.2907 20.2618	20.7763
3 "	604 633	10564000 10466000	20436000 19955000	2755000 2805000	1.9345 1.9067	7.4178 7.1141	26.2590 25.8811	26.0701	25.3775 24.3156	24.8465
4 (a) "	605 634	3724300 3794800	270090 257010	2755000 949650	0.0725 0.0677	0.0980 0.2706	0.9844 0.9193	0.9519	-0.2168 0.3867	0.0849
5 "	606 635	17437000 16952000	8657800 8314100	4744000 4624500	0.4965 0.4904	1.8250 1.7978	6.7398 6.6574	6.6986	5.8217 5.7267	5.7742
6 "	607 636	7226300 7840000	4374100 4583500	1786400 2060600	0.6053 0.5846	2.4486 2.2244	8.2164 7.9358	8.0761	8.0020 7.2181	7.6101
7 "	608 637	17922000 18227000	5619900 5537300	4919600 5249300	0.3136 0.3038	1.1423 1.0549	4.2565 4.1236	4.1901	3.4347 3.1288	3.2818
8 "	609 638	14050000 13819000	2244700 2080500	3788500 3887200	0.1598 0.1506	0.5925 0.5352	2.1687 2.0436	2.1062	1.5121 1.3118	1.4120
9 " "	610 612 639	12831000 4822200 5365700	4122700 1622700 1770800	3213300 1136700 1213500	0.3213 0.3365 0.3300	1.2830 1.4276 1.4593	4.3615 4.5678 4.4798	4.4697	3.9266 4.4320 4.5428	4.3005
10 (a) "	613 640	6272600 5827800	392810 353140	1464400 1308100	0.0626 0.0606	0.2682 0.2700	0.8501 0.8225	0.8363	0.3783 0.3844	0.3813

(a) Sample spilled during evaporation to dryness using nitrogen

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

Table XIV.9 GC/ECD Data for MX Standard Curve (for pH 8 Isotherm)

Experiment No.: EXP-89.MX.VI-5

SAMPLE	RUN NO.	MX CONC. (µg/µL)	MX VOL. (µL)	MX STD. (µg)	EMX STD. (µg)	MX/MBA Mass Ratio	EMX/MBA Mass Ratio	MX/TCT Mass Ratio	EMX/TCT Mass Ratio	MBA Area Counts	MX Area Counts	TCT Area Counts	MX/MBA Area Ratio	MX/TCT Area Ratio
STD 66.512 ng	616	0.033256	2.0	0.0641	0.0025	0.0402	0.0015	21.4	0.8	13695000	404450	2748200	0.0295	0.1472
"	641	0.033256	2.0	0.0641	0.0025	0.0402	0.0015	21.4	0.8	9858700	168410	2269400	0.0171	0.0742
"	644	0.033256	2.0	0.0641	0.0025	0.0402	0.0015	21.4	0.8	10826000	180390	2536400	0.0167	0.0711
STD 332.56 ng	617	0.033256	10.0	0.3203	0.0123	0.2008	0.0077	106.8	4.1	3717700	592300	699870	0.1593	0.8463
"	642	0.033256	10.0	0.3203	0.0123	0.2008	0.0077	106.8	4.1	4124000	643080	813920	0.1559	0.7901
"	651	0.033256	10.0	0.3203	0.0123	0.2008	0.0077	106.8	4.1	2855700	445050	611890	0.1558	0.7273
STD 997.68 ng	618	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	2113600	510170	1735800	0.2414	0.2939
"	650	0.33256	3.0	0.9608	0.0369	0.6024	0.0231	320.3	12.3	1610100	354730	1680700	0.2203	0.2111
STD 1995.36 ng	619	0.33256	6.0	1.9216	0.0738	1.2047	0.0463	640.5	24.6	6878200	2867600	2267300	0.4169	1.2648
"	652	0.33256	6.0	1.9216	0.0738	1.2047	0.0463	640.5	24.6	4558700	1726800	1711400	0.3788	1.0090
STD 9976.8 ng	620	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	19907000	19559000	6803100	0.9825	2.8750
"	653	3.3256	3.0	9.6077	0.3691	6.0236	0.2314	3202.6	123.0	18186000	15940000	6921200	0.8765	2.3031
STD 49884 ng	621	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	13266000	55971000	3836900	4.2191	14.5876
"	654	3.3256	15.0	48.0383	1.8457	30.1181	1.1572	16012.8	615.2	12794000	49930000	3829400	3.9026	13.0387
STD 99768 ng	623	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	5079800	38324000	1267700	7.5444	30.2311
"	656	33.256	3.0	96.0766	3.6914	60.2361	2.3144	32025.5	1230.5	4970700	37934000	1297400	7.6315	29.2385

MBA Conc. = 0.1595 µg/µL
MBA Mass = 1.595 µg
TCT Conc. = 0.0003 µg/µL
TCT Mass = 0.003 µg

MBA+TCT Mixture Vol. = 10.0 µL

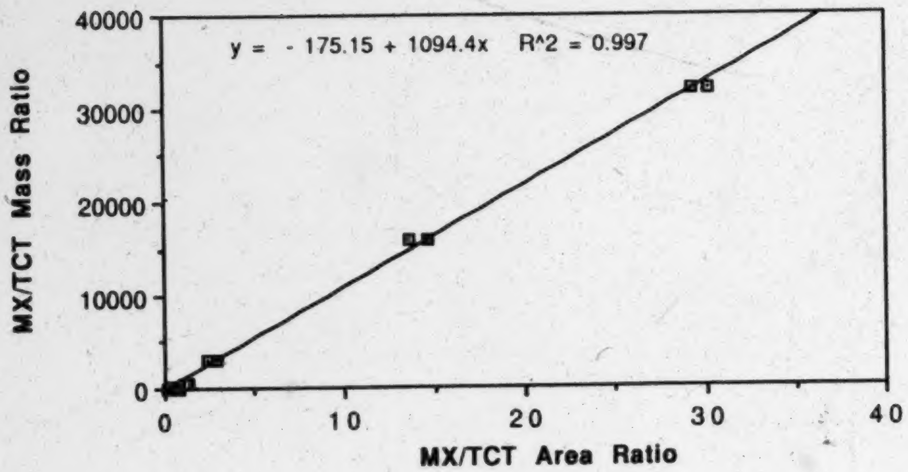


Figure XIV.3 MX Calibration Using TCT Internal Standard (for pH 8 Isotherm)

Appendix XV

GC/ECD Response Data For Adsorption/Desorption Experiments

Table XV.1 Example of Typical Standard Preparation and GC/ECD Analysis

Experiment No.: AD-88-1

Standards prepared in EtOAc

Sample	Run No.	MX Conc. (µg/L)	MX Vol. (µL)	Mass Mx (µg)	Mass EMX (µg)	Mass MBA (µg)	Mass Ratio		Area Counts			Area Ratio	
							MX/MBA	EMX/MBA	MBA	MX	EMX	MX/MBA	EMX/MBA
						LOW RANGE STANDARDS							
Std 12.25 ng	330	0.01225	1.0	0.0085	0.0038	1.305	0.0065	0.0029	508030	23491	27952	0.0462	0.0550
=	343	0.01225	1.0	0.0085	0.0038	1.305	0.0065	0.0029	450890	21119	14761	0.0468	0.0327
Std 49.0 ng	344	0.01225	4.0	0.0338	0.0152	1.305	0.0259	0.0116	738280	39434	24174	0.0534	0.0327
=	345	0.01225	4.0	0.0338	0.0152	1.305	0.0259	0.0116	890870	46083	28619	0.0517	0.0321
Std 122.5 ng	316	0.01225	10.0	0.0845	0.0380	1.305	0.0648	0.0291	790500	58533	35941	0.0740	0.0455
=	348	0.01225	10.0	0.0845	0.0380	1.305	0.0648	0.0291	8292340	62618	42500	0.0076	0.0051
Std 245 ng	332	0.245	1.0	0.1691	0.0760	1.305	0.1295	0.0582	12300	1014	8842	0.0824	0.71[illegible]
Std 980 ng	314	0.245	4.0	0.6762	0.3038	1.305	0.5182	0.2328	449770	246190	169310	0.5474	0.3764
=	359	0.245	4.0	0.6762	0.3038	1.305	0.5182	0.2328	22371	10528	47024	0.4706	2.1020
=	360	0.245	4.0	0.6762	0.3038	1.305	0.5182	0.2328	23621	7966	47232	0.3372	1.9986
						HIGH RANGE STANDARDS							
Std 114900 ng	349	11.49	10.0	79.28	35.62	1.305	60.7517	27.2943	465400	18192000	13443000	39.0890	28.8848
=	374	11.49	10.0	79.28	35.62	1.305	60.7517	27.2943	510820	18811000	14044000	36.8251	27.4931
Std 229800 ng	350	11.49	20.0	158.56	71.24	1.305	121.5034	54.5885	972170	35620000	22820000	36.6397	23.4733
=	357	11.49	20.0	158.56	71.24	1.305	121.5034	54.5885	1469500	50998000	31603000	34.7043	21.5060
Std 459600 ng	355	11.49	40.0	317.1	142.5	1.305	243.0069	109.1770	714930	46127000	30680000	64.5196	42.9133
=	356	11.49	40.0	317.1	142.5	1.305	243.0069	109.1770	722790	46469000	30890000	64.2911	42.7372
Std 1149 µg	353	114.9	10.0	792.8	356.2	1.305	607.5172	272.9425	243280	40471000	27873000	166.3556	114.5717
=	354	114.9	10.0	792.8	356.2	1.305	607.5172	272.9425	346450	51310000	36698000	148.1022	105.9258

Table XV.2 Data Used in Comparison of MX/MBA Response for Two Different Concentration Methods Prior to Derivatization (Experiment AD-88-3)

ExperimentNo.: AD-88-3 **Comparison of derivatizing in EtOAc vs Dryness**

STANDARDS DERIVATIZED IN 0.5 mL EtOAc

Sample	Run No.	MX Conc. (µg/µL)	MX Vol. (µL)	Mass MX (µg)	Mass EMX (µg)	MBA Vol. (µL)	MBA Conc. (µg/µL)	Mass MBA (µg)	Mass Ratio MX/MBA	Mass Ratio EMX/MBA	Area Counts MBA	Area Counts MX	Area Counts EMX	Area Ratio MX/MBA	Area Ratio EMX/MBA
Std EtOAc 114.9 µg	625	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	14463000	28917000	9091100	1.9994	0.6286
"	648	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	17024000	34474000	10709000	1.9561	0.6076
"	2	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	29911000	56543000	17801000	1.9212	0.6157
Std EtOAc 1149 µg	649	114.9	10.0	1113.4	35.6	10.0	0.1306	1.306	853.2	27.3	691350	5256800	1193600	7.6022	1.7266
"	3	114.9	10.0	1113.4	35.6	10.0	0.1306	1.306	853.2	27.3	1752800	17942000	9205600	10.2362	5.2519
StdEtOAc 1723.5µg	630	114.9	15.0	1670.1	53.4	10.0	0.1306	1.306	1279.7	40.9	3926600	71999000	29017000	18.3274	7.3983
"	660	114.9	15.0	1670.1	53.4	10.0	0.1306	1.306	1279.7	40.9	4871400	78662000	31077000	16.1272	6.3796
"	4	114.9	15.0	1670.1	53.4	10.0	0.1306	1.306	1279.7	40.9	4583000	82390000	31399000	17.9773	6.8512
StdEtOAc 2298µg	632	114.9	20.0	2226.8	71.2	10.0	0.1306	1.306	1706.3	54.6	1626100	95071000	37906000	58.4657	23.3110
"	5	114.9	20.0	2226.8	71.2	10.0	0.1306	1.306	1706.3	54.6	2529600	66819000	31110000	26.0196	12.2984
"	6	114.9	20.0	2226.8	71.2	10.0	0.1306	1.306	1706.3	54.6	2756600	67327000	33049000	24.4248	11.9896
StdEtOAc 2872.5µg	633	114.9	25.0	2783.5	89.0	10.0	0.1306	1.306	2132.9	68.2	2097400	64224000	21035000	30.6206	10.0291
"	662	114.9	25.0	2783.5	89.0	10.0	0.1306	1.306	2132.9	68.2	2094800	104960000	27445000	50.1146	13.1015

STANDARDS DERIVATIZED DRY

Sample	Run No.	MX Conc. (µg/µL)	MX Vol. (µL)	Mass MX (µg)	Mass EMX (µg)	MBA Vol. (µL)	MBA Conc. (µg/µL)	Mass MBA (µg)	Mass Ratio MX/MBA	Mass Ratio EMX/MBA	Area Counts MBA	Area Counts MX	Area Counts EMX	Area Ratio MX/MBA	Area Ratio EMX/MBA
Std Dry 114.9 µg	634	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	6378600	11059000	43362	1.7337	0.0068
"	663	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	5104800	8557300	38621	1.6763	0.0076
"	9	114.9	1.0	111.3	3.6	10.0	0.1306	1.306	85.3	2.7	4723300	7900900	30929	1.6727	0.0065
Std Dry 1149 µg	655	114.9	10.0	1113.4	35.6	10.0	0.1306	1.306	853.2	27.3	4436480	54936500	12504	12.3830	0.0028
	656	114.9	10.0	1113.4	35.6	10.0	0.1306	1.306	853.2	27.3	4121300	53946000	8162	13.0896	0.0020
"	10	114.9	10.0	1113.4	35.6	10.0	0.1306	1.306	853.2	27.3	4751600	55927000	16840	11.7701	0.0035
Std Dry 1723.5 µg	657	114.9	15.0	1670.1	53.4	10.0	0.1306	1.306	1279.7	40.9	2183100	41807000	35614	19.1503	0.0163
"	11	114.9	15.0	1670.1	53.4	10.0	0.1306	1.306	1279.7	40.9	1660400	24490000	47464	14.8368	0.0286
Std Dry 2298 µg	658	114.9	20.0	2226.8	71.2	10.0	0.1306	1.306	1706.3	54.6	402530	13687000	76403	34.0024	0.1898
Std Dry 2872.5 µg	660	114.9	25.0	2783.5	89.0	10.0	0.1306	1.306	2132.9	68.2	2263200	7[illegible]5000	3604	31.4179	0.0017
"	13	114.9	25.0	2783.5	89.0	10.0	0.1306	1.306	2132.9	68.2	1589100	41596000	86991	26.1771	0.0547

MX: 96.9%
EMX: 3.1%

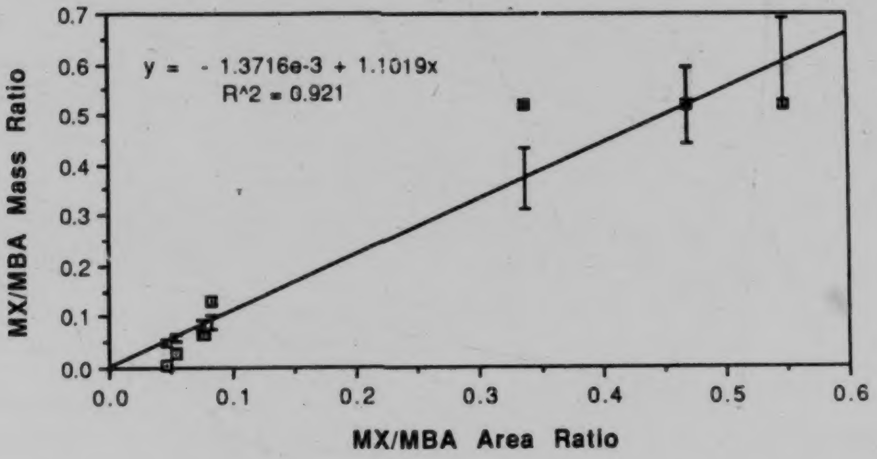


Figure XV.1 Low Range MX Response Curve Used in Experiment AD-88-1.

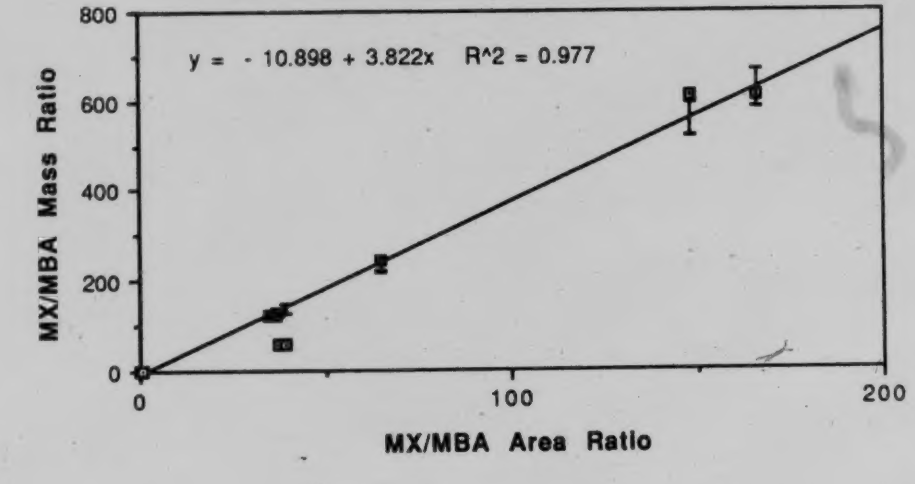


Figure XV.2 High Range MX Response Curve Used in Experiment AD-88-1.

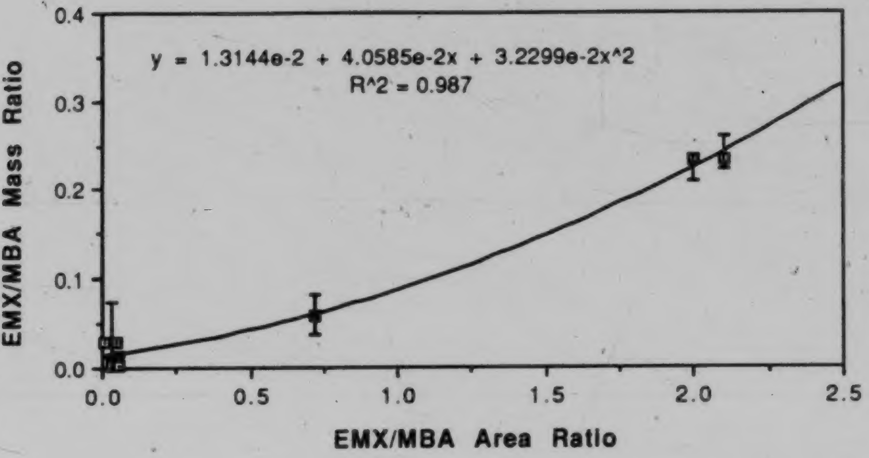


Figure XV.3 Low Range EMX Response Curve Used for All Adsorption/Desorption Experiments.

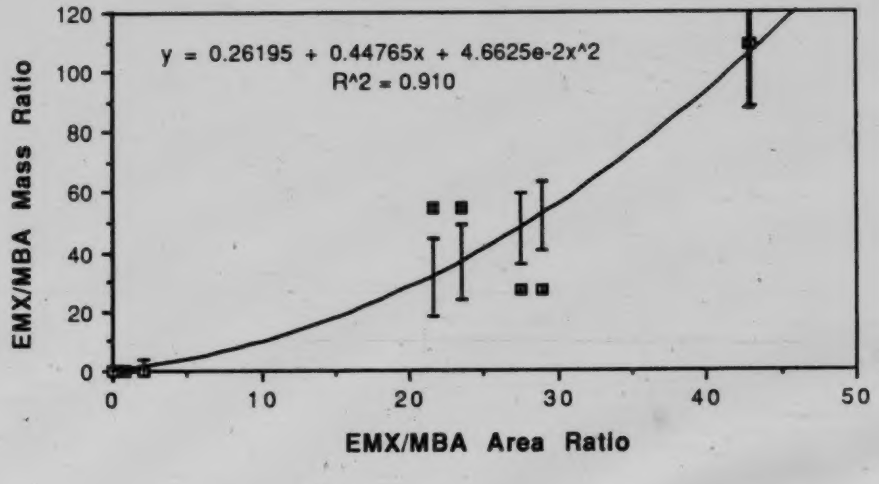


Figure XV.4 High Range EMX Response Curve Used for All Adsorption/Desorption Experiments.

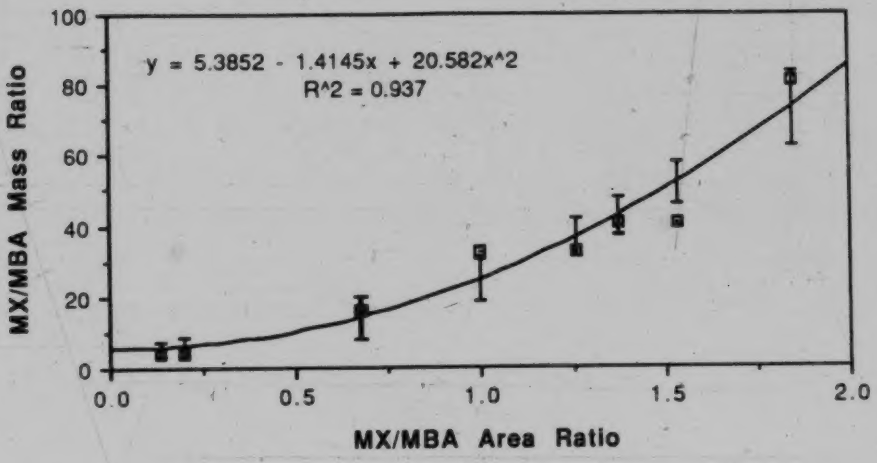


Figure XV.5 Low Range MX Response Curve Used in Experiments AD-88-3 and AD-88-4.

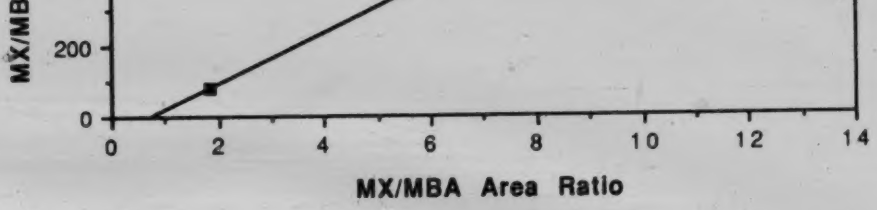


Figure XV.6 High Range MX Response Curve Used in Experiments AD-88-1 and AD-88-4.

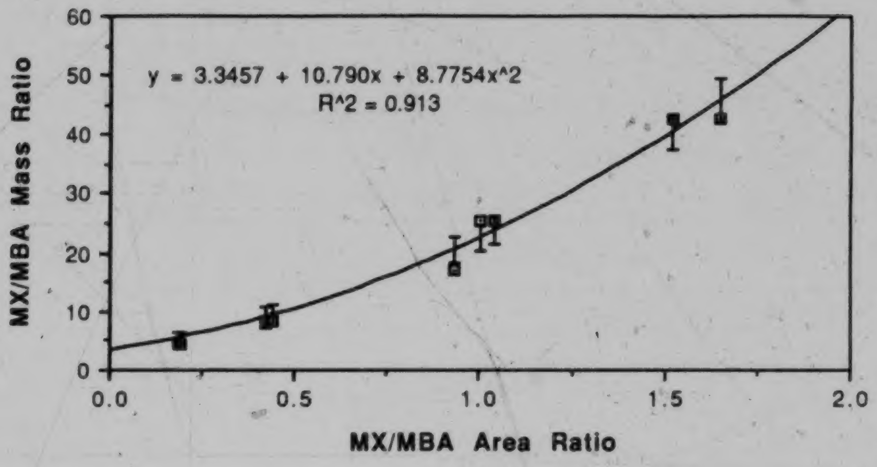


Figure XV.7 Low Range Large Volume Derivatization (LVD) MX Response Curve Used in Experiment AD-88-4 Desorption Calculations.

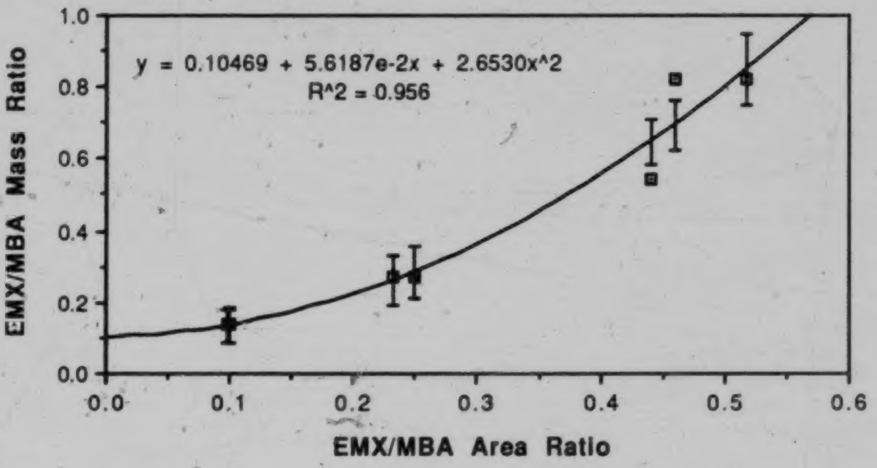


Figure XV.8 Low Range Large Volume Derivatization (LVD) EMX Response Curve Used in Experiment AD-88-4 Desorption Calculations.

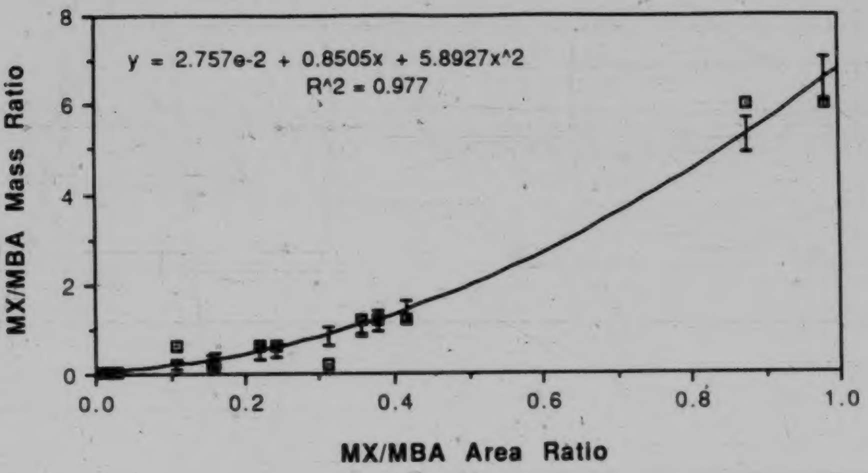


Figure XV.9 Low Range MX Response Curve Used in Experiments AD-89-5 and AD-89-6.

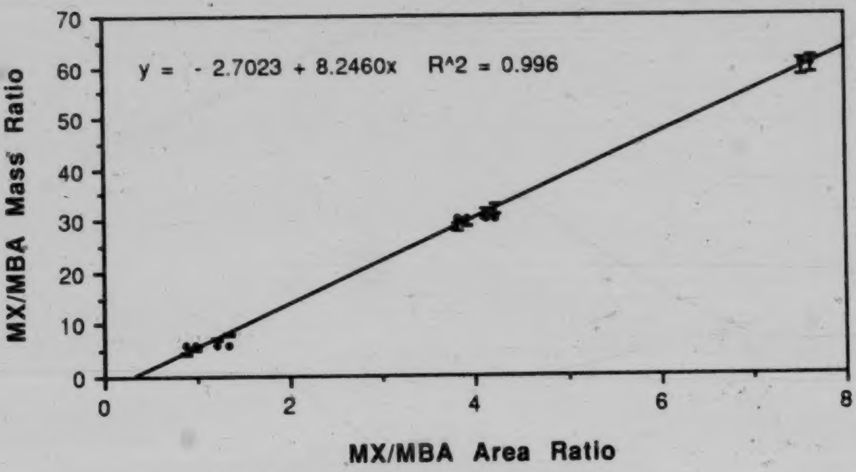


Figure XV.10 High Range MX Response Curve Used in Experiments AD-89-5 and AD-89-6.

Appendix XVI

Adsorption/Desorption Investigation Results

Table XVI.1 MX and EMX Present Following Initial Adsorption Step (Expt. AD-88-1)

Experiment No.: AD-88-1

Water extraction with EtOAc (150ml water; 37, 22, 22 mL EtOAc)
Extracts derivatized in 0.5 mL solvent.

Sample	Run No.	Mass MBA (µg)	Area Counts			Area Ratio		MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
1B H2O Ext •	298 380	1.305 1.305	1872500 1497000	23785000 22084000	18250000 16994000	12.7023 14.7522	9.7463 11.3520	52.409 63.315	57.862	12.608 15.809	14.209
2 H2O Ext •	300 301	1.305 1.305	587980 441240	24403 9711	27638 14856	0.0415 0.0220	0.0470 0.0337	0.062 0.032	0.047	0.021 0.020	0.021
3 H2O Ext •	302 303	1.305 1.305	811710 779680	31854 30741	24086 23898	0.0392 0.0394	0.0296 0.0307	0.059 0.059	0.059	0.020 0.020	0.020
4 H2O Ext •	304 366	1.305 1.305	1776400 1725300	14416 13434	60817 23631	0.0081 0.0078	0.0342 0.0137	0.011 0.010	0.010	0.020 0.019	0.020
5B H2O Ext •	318 369	1.305 1.305	1843500 1989700	25336000 27440000	13273000 14773000	13.7434 13.7910	7.1999 7.4247	57.948 58.201	58.075	8.219 8.573	8.396
6 H2O Ext •	319 370	1.305 1.305	1508200 1744600	27387 32899	27387 57503	0.0182 0.0189	0.0182 0.0330	0.026 0.027	0.027	0.019 0.020	0.020
7 H2O Ext •	320 371	1.305 1.305	1717800 1974800	9301 9297	47721 19801	0.0054 0.0047	0.0278 0.0100	0.006 0.005	0.006	0.020 0.019	0.019
8 H2O Ext •	305 372	1.305 1.305	389080 384550	3044 2799	16232 13802	0.0078 0.0073	0.0417 0.0359	0.010 0.009	0.010	0.021 0.020	0.021
9B H2O Ext •	373	1.305	2611100	29774000	18503000	11.4029	7.0863	45.496	45.496	8.043	8.043
10 H2O Ext Blank •	306 378	1.305 1.305	1328100 1265100	5731 5482	4527 7251	0.0043 0.0043	0.0034 0.0057	0.005 0.005	0.005	0.018 0.019	0.019
11 H2O Ext (b) (100 ng/L)	307 376	1.305 1.305	1614900 1765200	9967 13728	32606 18492	0.0062 0.0078	0.0202 0.0105	0.008 0.010	0.009	0.019 0.019	0.019
12 H2O Ext (c) (500 ng/L)	308 379	1.305 1.305	1655500 2033800	28817 33286	21567 25812	0.0174 0.0164	0.0130 0.0127	0.025 0.023	0.024	0.019 0.019	0.019

(a) Based upon extraction of 150 mL sample; corrected to total bottle volume of 160 mL.
(b) Spiked with 100 ng/L MX+EMX; (11.04 ng MX, 4.96 ng EMX in 160 mL)
(c) Spiked with 500 ng/L MX+EMX; (55.20 ng MX, 24.8 ng EMX in 160 mL)

Spike contained MX: 69.0 %
EMX: 31.0 %

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-13.5 mg, #3-12.4 mg, #4-19.1 mg, #6-19.2 mg, #7-29.6 mg, #8-29.7 mg.

Table XVI.2 MX and EMX Present Following First Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No.: AD-88-1

First carbon extraction with EtOAc (150 mL).
Analysis of 150 mL sample.
Extracts derivatized in 0.5 mL solvent.

Sample	Run No.	Mass MBA (µg)	Area Counts			Area Ratio		MX (µg)	MX Avg (µg)	EMX (µg)	EMX Avg (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
1B C/EA Ext (1)	311	1.305	281250	1267400	504800	4.5063	1.7948	8.254		1.587	
•	388	1.305	301840	1207200	468990	3.9995	1.5538	5.726	6.990	1.397	1.492
2 C/EA Ext (1)	309	1.305	336760	18809	24276	0.0559	0.0721	0.079		0.021	
•	367	1.305	368700	30355	NAR	0.0823	NC	0.117	0.098	NC	0.021
3 C/EA Ext (1)	322	1.305	863520	35800	84548	0.0415	0.0979	0.058		0.023	
•	415	1.305	1004800	22192	105970	0.0221	0.1055	0.030	0.044	0.023	0.023
4 C/EA Ext (1)	310	1.305	1100100	23346	45089	0.0212	0.0410	0.029		0.019	
•	416	1.305	1525200	35132	NAR	0.0230	NC	0.032	0.030	NC	0.019
5B C/EA Ext (1)	323	1.305	411970	1402900	401970	3.4053	0.9757	4.927		0.970	
•	413	1.305	546580	1532300	435670	2.8034	0.7971	4.055	4.491	0.847	0.908
6 C/EA Ext (1)	324	1.305	754840	41617	58988	0.0551	0.0781	0.078		0.022	
•	417	1.305	755140	30954	98773	0.0410	0.1308	0.058	0.068	0.025	0.023
7 C/EA Ext (1) (a)	325	1.305	1208400	27877	47877	0.0231	0.0397	0.032		0.019	
•	418	1.305	1181900	26965	NAR	0.0228	NC	0.031	0.031	NC	NC
8 C/EA Ext (1)	312	1.305	1094700	49018	65213	0.0448	0.0596	0.063		0.020	
•	419	1.305	1037900	51503	NAR	0.0496	NC	0.070	0.067	NC	0.020
9B C/EA Ext (1)	326	1.305	1372300	2220100	767390	1.6178	0.5592	2.340		0.688	
•	414	1.305	1585100	2424000	846740	1.5292	0.5342	2.211	2.275	0.672	0.680
10 C/EA Ext (1)	329	1.305	1795700	5716	14761	0.0032	0.0082	0.003		0.018	
(Blank)	420	1.305	1685900	6025	5906	0.0036	0.0035	0.003	0.003	0.017	0.017
11 C/EA Ext (1)	327	1.305	1842900	8145	12331	0.0044	0.0067	0.005		0.018	
(100 ng/L)	421	1.305	1458500	2858	2597	0.0020	0.0018	0.001	0.003	0.017	0.017
12 C/EA Ext (1)	328	1.305	1614500	2639	11248	0.0016	0.0070	0.001		0.018	
(500 ng/L)	422	1.305	1040000	NAR	1967	NC	0.0019	NC	NC	0.017	0.018

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

(a) Sample spilled prior to derivatization, approx. 40 mL lost.

Table XVI.4 MX and EMX Present Following Third Desorption Using Methanol (Expt. AD-88-1)

ExperimentNo.: 88-AD-1

Third carbon extraction, using MeOH (300ml)
Analysis of 300 mL sample.
Extracts derivatized in 0.5 mL solvent.

Sample	Run No.	MassMBA (µg)	Area Counts			Area Ratio		MX (µg)	MX Avg (µg)	EMX (µg)	EMX Avg (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
2 MeOH/EA •	388 402	1.305 1.305	527680 501710	6916 9845	26927 20065	0.0131 0.0196	0.0510 0.0400	0.017 0.027	0.022	0.020 0.019	0.020
3 MeOH/EA •	389 403	1.305 1.305	299490 192400	11674 5941	20456 16808	0.0390 0.0309	0.0683 0.0874	0.055 0.043	0.049	0.021 0.022	0.022
4 MeOH/EA •	390 404	1.305 1.305	729340 1202800	20779 32672	27448 38491	0.0285 0.0272	0.0376 0.0320	0.039 0.038	0.038	0.019 0.019	0.019
6 MeOH/EA •	393 405	1.305 1.305	1330500 1139300	38198 29971	30427 20807	0.0287 0.0263	0.0229 0.0183	0.040 0.036	0.038	0.018 0.018	0.018
8 MeOH/EA •	381 407	1.305 1.305	1211400 1269900	19949 13860	11434 21204	0.0165 0.0109	0.0094 0.0167	0.022 0.014	0.018	0.018 0.018	0.018

Sample #7 MeOH/EA not included in MeOH extraction since spilled prior to derivatization in first carbon extraction, approx. 40 mL lost.

Table XVI.3 MX and EMX Present Following Second Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No. : AD-88-1

Second carbon extraction with EtOAc (300ml)
Analysis of 250 mL of the 300 mL sample.
Extracts derivatized in 0.5 mL solvent.

Sample	Run No.	Mass MBA (µg)	Area Counts			Area Ratio		MX (µg)	MX Avg (µg)	EMX (µg)	EMX Avg (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
2 C/EA Ext (2) •	334 383	1.305 1.305	128100 211350	75334 89862	78830 47976	0.5881 0.4252	0.6154 0.2270	1.019 0.736	0.878	0.079 0.038	0.058
3 C/EA Ext (2) •	335 363	1.305 1.305	325850 402790	244070 202650	139780 99581	0.7490 0.5031	0.4290 0.2472	1.299 0.872	1.085	0.057 0.039	0.048
4 C/EA Ext (2) •	336 364	1.305 1.305	190920 556420	136850 430180	182110 382540	0.7168 0.7731	0.9539 0.6875	1.243 1.340	1.292	0.127 0.088	0.108
6 C/EA Ext (2) •	337 365	1.305 1.305	364860 430820	131860 128870	51629 105420	0.3614 0.2991	0.1415 0.2447	0.625 0.517	0.571	0.031 0.039	0.035
7 C/EA Ext (2) (a)	338 384	1.305 1.305	149800 189000	13581 2083	NAR NAR	0.0907 0.0110	NC NC	0.155 0.017	0.086	NC NC	NC NC
8 C/EA Ext (2) •	339 385	1.305 1.305	163180 342200	30024 22001	NAR 99487	0.1840 0.0643	NC 0.2907	0.317 0.110	0.213	NC 0.043	NC 0.043

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

(a) Sample spilled prior to derivatization in first carbon extraction, approx. 40 mL lost.

Table XVI.6 EMX Recovered Following First Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No. : AD-88-1 EMX Desorption Recovery Results-First extraction using EtOAc

Sample	Mass EMX (ug)		Water Present in Carbon Extr. (mL)	MX Pres. in Extran. Water (ug)	Net EMX Recovered From Carbon (ug) (a)	Min.EMX Recovered	Max.EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,9B EtOAc Ext.	10.218	1.027	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.021	0.021	10.0	0.0013	0.020	.04	0.19
3 C Ext. (EtOAc)	0.020	0.023	10.0	0.0013	0.022	.04	0.21
4 C Ext. (EtOAc)	0.020	0.019	10.0	0.0013	0.018	.04	0.17
6 C Ext. (EtOAc)	0.020	0.023	10.0	0.0013	0.022	.04	0.21
8 C Ext. (EtOAc)	0.020	0.020	10.0	0.0013	0.019	.04	0.18

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Based on calculated mass of initial EMX spike.
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

NA: Not applicable to blank sample which contained no carbon

Table XVI.8 EMX Recovered Following Second Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No. : AD-88-1 EMX Desorption Recovery Results-Second extraction using EtOAc

Sample	Mass EMX (µg)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (µg)	Net EMX Recovered From Carbon (µg) (a)	Min.EMX Recovered (%) (b)	Max.EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,8B EtOAc Ext.	10.216	NA	NA	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.021	0.058	NA	NA	0.058	0.12	0.57
3 C Ext. (EtOAc)	0.020	0.048	NA	NA	0.048	0.10	0.47
4 C Ext. (EtOAc)	0.020	0.108	NA	NA	0.108	0.22	1.06
6 C Ext. (EtOAc)	0.020	0.035	NA	NA	0.035	0.07	0.34
8 C Ext. (EtOAc)	0.020	0.043	NA	NA	0.043	0.09	0.42

NA: Not applicable

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Based on calculated mass of initial EMX spike
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration

Table XVI.5 MX Recovery Following First Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No. : AD-88-1 MX Desorption Recovery Results-First extraction using EtOAc

Sample	Mass MX (µg)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (µg)	Net MX Recovered From Carbon (µg) (a)	Min. MX Recovered (%) (b)	Max. MX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,6B EtOAc Ext.	53.811	4.585	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.047	0.098	10.0	0.0029	0.095	0.09	0.18
3 C Ext. (EtOAc)	0.059	0.044	10.0	0.0037	0.040	0.04	0.07
4 C Ext. (EtOAc)	0.010	0.030	10.0	0.0006	0.029	0.03	0.05
5 C Ext. (EtOAc)	0.027	0.068	10.0	0.0017	0.066	0.06	0.12
6 C Ext. (EtOAc)	0.010	0.067	10.0	0.0006	0.066	0.06	0.12

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Based on calculated mass of initial MX spike.
(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

NA: Not applicable to blank sample which contained no carbon

Table XVI.7 MX Recovered Following Second Desorption Using Ethyl Acetate (Expt. AD-88-1)

Experiment No. : AD-88-1 MX Desorption Recovery Results-First extraction using EtOAc

Sample	Mass MX (µg)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (µg)	Net MX Recovered From Carbon (µg) (a)	Min. MX Recovered (%) (b)	Max. MX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,8B EtOAc Ext	53.811	NA	NA	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.047	0.878	10.0	0.0029	0.875	0.79	1.63
3 C Ext. (EtOAc)	0.059	1.085	10.0	0.0037	1.081	0.98	2.01
4 C Ext. (EtOAc)	0.010	1.292	10.0	0.0006	1.291	1.17	2.40
6 C Ext. (EtOAc)	0.027	0.571	10.0	0.0017	0.569	0.52	1.06
8 C Ext. (EtOAc)	0.010	0.213	10.0	0.0006	0.212	0.19	0.39

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Based on calculated mass of initial MX spike.
(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

NA Not applicable to blank sample which contained no carbon

Table XVI.9 MX Recovered Following Third Desorption Using Methanol (Expt. AD-88-1)

Experiment No. : AD-88-1 MX Desorption Recovery Results-Third extraction using MeOH

Sample	Mass MX (µg)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (µg)	Net MX Recovered From Carbon (µg) (a)	Min. MX Recovered (%) (b)	Max. MX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,9B EtOAc Ext.	53.811	NA	NA	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.047	0.022	NA	NA	0.022	0.02	0.04
3 C Ext. (EtOAc)	0.059	0.049	NA	NA	0.049	0.04	0.09
4 C Ext. (EtOAc)	0.010	0.038	NA	NA	0.038	0.03	0.07
6 C Ext. (EtOAc)	0.027	0.038	NA	NA	0.038	0.03	0.07
8 C Ext. (EtOAc)	0.010	0.018	NA	NA	0.018	0.02	0.03

NA: Not applicable

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Based on calculated mass of initial MX spike.
(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

Table XVI.10 EMX Recovered Following Third Desorption Using Methanol (Expt. AD-88-1)

Experiment No. : AD-88-1 EMX Desorption Recovery Results-Third extraction using MeOH

Sample	Mass EMX (µg)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (µg)	Net EMX Recovered From Carbon (µg) (a)	Min.EMX Recovered (%) (b)	Max.EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
Avg. 1B,5B,6B EtOAc Ext.	10.216	NA	NA	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.021	0.020	NA	NA	0.020	0.040	0.20
3 C Ext. (EtOAc)	0.020	0.022	NA	NA	0.022	0.044	0.22
4 C Ext. (EtOAc)	0.020	0.019	NA	NA	0.019	0.038	0.19
5 C Ext. (EtOAc)	0.020	0.018	NA	NA	0.018	0.036	0.18
6 C Ext. (EtOAc)	0.020	0.018	NA	NA	0.018	0.036	0.18

NA: Not applicable

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Based on calculated mass of initial EMX spike.
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

Table XVI.11 MX and EMX Present Following Initial Adsorption Step (Expt. AD-88-3)

Experiment No. : AD-88-3 Water extraction with EtOAc (150 mL water; 37, 22, 22 mL EtOAc)

Date : November 15,1988

Sample	Run No.	Mass MBA	Area Counts			Area Ratio		MX (a)	MX Avg (a)	EMX (a)	EMX Avg (a)
		(µg)	MBA	MX	EMX	MX/MBA	EMX/MBA	(µg)	(µg)	(µg)	(µg)
1B H2O Ext.	497	1.305	2271900	63461000	44609	27.9330	0.0196	2716.344	2716.344	0.019	0.019
2 H2O Ext. " "	449 470 505	1.305 1.305 1.305	1297300 1274900 1032400	354210 444230 289220	NAR NAR 560	0.2730 0.3484 0.2801	NC NC 0.0005	9.103 10.297 9.201	9.534	NC NC 0.018	NC NC 0.018
3 H20 Ext. "	450 472	1.305 1.305	3558400 887520	533500 96053	15563 7856	0.1500 0.1082	0.0044 0.0089	7.853 7.626	7.740	0.018 0.019	0.018
4 H2O Ext. "	451 473	1.305 1.305	1706000 1576100	445260 331110	NAR NAR	0.2610 0.2101	NC NC	8.942 8.355	8.648	NC NC	NC NC
5 H20 Ext. "	452 474	1.305 1.305	1135900 1141800	306940 246340	NAR NAR	0.2702 0.2157	NC NC	9.064 8.413	8.739	NC NC	NC NC

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

Spike contained MX:96.9%
EMX:3.1%

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-11.12 mg, #3-9.04 mg, #4-10.73 mg, #5-9.14 mg.

Table XVI.12 MX and EMX Present Following Desorption Using Various Solvents (Expt. AD-88-3)

ExperimentNo.: AD-88-3

Carbon desorption with various solvents.
Analysis of 10 mL of the (25 mL + 10 mL) samples & blank.
Extracts derivalized dry.

Sample	RunNo.	MassMBA (µg)	Area Counts			Area Ratio		Water Present(mL	MX (a) (µg)	MX Avg (a) (µg)	EMX (a) (µg)	EMX Avg (a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA					
1B C Ext.(EtOAc)	464	1.305	13357000	41824000	127900	3.1312	0.0096	10.0	773.688	683.755	0.062	0.062
"	494	1.305	13325000	36370000	162410	2.7295	0.0122	10.0	641.832		0.062	
"	506	1.305	13564000	37298000	170240	2.7498	0.0126	10.0	648.501		0.062	
"	511	1.305	11560000	32580000	163020	2.8183	0.0141	10.0	671.001		0.062	
2 C Ext.(EtOAc)	465	1.305	16144000	22217000	224040	1.3762	0.0139	10.0	193.778	182.347	0.062	0.062
"	495	1.305	16266000	21335000	230610	1.3116	0.0142	10.0	177.886		0.062	
"	507	1.305	17078000	22221000	211810	1.3011	0.0124	10.0	175.376		0.062	
3 C Ext.(Acetone)	466	1.305	16703000	22941000	1396800	1.3735	0.0836	10.0	137.924	122.857	0.076	0.084
"	496	1.305	9597000	10022000	1183200	1.0443	0.1233	10.0	120.402		0.085	
"	508	1.305	7905700	7821000	1143900	0.9893	0.1447	10.0	110.243		0.090	
		1.305										
4 C Ext.(DCM:MeOH)	467	1.305	13806000	18067000	203400	1.3086	0.0147	10.0	126.548	134.864	0.063	0.063
"	499	1.305	15229000	17633000	227180	1.1579	0.0149	10.0	143.180		0.063	
5 C Ext.(DCM:MeOH)	468	1.305	6233100	3460300	128410	0.5551	0.0206	10.0	50.013	50.013	0.064	0.064
+Displacer (b)	502	1.305	5417100	2433200	95587	0.4492	0.0176	10.0	29.065		0.063	

(a) Not corrected for volume of water present as supernatent during desorption step.
(b) Sample filtered twice over Na2SO4 to remove benz(a)anthracene.

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

Table XVI.13 MX Recovery Following Desorption Using Various Solvents (Expt. AD-88-3)

Experiment No. : AD-88-3 MX Desorption Recovery Results

Sample	Mass MX (ug)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (ug)	Net MX Recovered From Carbon (ug) (a)	Min. MX Recovered (%) (b)	Max. MX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
1st C Ext. (EtOAc)	2716.344	683.755	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	9.534	182.347	10.0	0.5959	181.751	5.80	6.71
3 C Ext. (Acetone)	7.740	122.857	10.0	0.4838	122.373	3.90	4.52
5 C Ext. (50%DCM/MeOH)	8.648	134.864	10.0	0.5405	134.324	4.29	4.96
5 C Ext. (d) (50%DCM/MeOH)	8.739	50.013	10.0	0.5462	49.467	1.58	1.83

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Based on calculated mass of initial MX spike.
(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.
(d) Included 0.5008 g benz(a)anthracene displacer.

NA: Not applicable to blank sample which contained no carbon

Table XVI.14 EMX Recovery Following Desorption Using Various Solvents (Expt. AD-88-3)

Experiment No. : AD-88-3 EMX Desorption Recovery Results

Sample	Mass EMX (μg)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (μg)	Net EMX Recovered From Carbon (μg) (a)	Min. EMX Recovered (%) (b)	Max. EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	0.019	0.082	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.019	0.082	10.0	0.0011	0.081	0.606	NR
3 C Ext. (Acetone)	0.019	0.084	10.0	0.0011	0.083	0.625	NR
4 C Ext. (50%DCM/MeOH)	0.000	0.083	10.0	0.0000	0.083	0.626	NR
4 C Ext. (d) (50%DCM/MeOH)	0.000	0.084	10.0	0.0000	0.084	0.636	NR

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Based on calculated mass of initial EMX spike.
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.
(d) Included 0.5008 g benz(a)anthracene displacer.

NA: Not applicable to blank sample which contained no carbon
NR: Not reported since final carbon extraction values exceed initial blank extraction value of 0.019 μg, which was much lower than expected

Table XVI.15 MX and EMX Present Following Initial Adsorption Step (Expt. AD-88-4)

Experiment No. : AD-88-4

Water extraction with EtOAc (150ml water; 37, 22, 22 mL EtOAc)
Extracts derivatized in 0.5 mL solvent, unless otherwise specified.

Sample	Run No.	Mass MBA (µg)	Area Counts			Area Ratio		MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg.(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
1B H2O Ext.	573	1.305	1384400	36930000	12463000	26.6758	9.0025	2590.6		10.908	
•	595	1.305	1194900	35180000	11599000	29.4418	9.7071	2867.2	2728.9	12.202	11.555
1B H2O Ext. (b)	574	1.305	2334100	50409000	51297	21.5968	0.0220	2082.6		0.019	
•	601	1.305	1400700	43868000	31964	31.3186	0.0228	3055.0		0.020	
•	602	1.305	1238200	42525000	29325	34.3442	0.0237	3357.6	2831.7	0.020	0.020
2 H2O Ext. (Spiked)	577	1.305	2263100	107580	41808	0.0475	0.0185	7.4743		0.019	
•	603	1.305	4503100	140360	46215	0.0312	0.0103	7.4695	7.4719	0.019	0.019
2 H2O Ext. (b)	578	1.305	4652500	155530	2255	0.0344	0.0005	7.4693		0.018	
•	604	1.305	4607900	143770	2257	0.0312	0.0005	7.4695	7.4694	0.018	0.018
3 H2O Ext.	580	1.305	17234000	423840	462880	0.0246	0.0269	7.4719		0.020	
•	605	1.305	14643000	403120	447830	0.0275	0.0306	7.4706	7.4712	0.020	0.020
4 H2O Ext. (Blank)	581	1.305	14814000	127000	124070	0.0086	0.0084	NC (c)		NC (d)	
•	606	1.305	12525000	92273	112920	0.0074	0.0090	NC (c)	NC (c)	NC (d)	NC (d)
5 H2O Ext.	582	1.305	10667000	552900	395400	0.0518	0.0371	7.4781		0.020	
•	607	1.305	7898300	397030	330130	0.0503	0.0418	7.4766	7.4774	0.021	0.021
6 H2O Ext. (Blank)	609	1.305	1682800	NAR	NAR	NC	NC	NC	NC	NC	NC

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.
(b) Sample taken to dryness prior to derivatization.
(c) Not calculated since GC/MS analysis comfirmed small peak was not MX
(d) Not calculated since GC/MS analysis comfirmed small peak was not EMX

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-11.0 mg, #3-10.9 mg, #5-9.6 mg, #6-10.8 mg.

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

Spike contained MX:96.9%
EMX:3.1%

Table XVI.16 MX and EMX Present Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-dione Displacer (Expt. AD-88-4)

Experiment No. : AD-88-4

Date: December 5,1988

Desorption with various solvents+displacer (25 mL).
Analysis of 10 mL of the (25 mL + 2 to 4 mL) sample (25 mL + 10 mL) blank. Extracts derivatized in 10 mL solvent.

Sample	Run No.	Mass MBA (µg)	Area Counts			Area Ratio		Water Present(mL)	MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg.(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA					
1B C Ext. (EtOAc)	586	1.305	21700000	21607000	7549700	0.9957	0.3479	10.0	104.1329		2.0343	
•	596	1.305	22583000	23495000	8785600	1.0404	0.3890	10.0	109.9818	107.0574	2.4120	2.2232
2 C Ext. (EtOAc)	592	1.305	10247000	1187800	619090	0.1159	0.0604	3.0	17.2422		0.4304	
•	597	1.305	9299300	1160600	575940	0.1248	0.0619	3.0	17.6613	17.4517	0.4325	0.4314
3 C Ext. (Acetone)	591	1.305	5824100	1889400	178410	0.3244	0.0306	2.4	27.7990		0.3894	
•	598	1.305	5255200	1872900	31378	0.3564	0.0060	2.4	29.7163		0.3759	
•	599	1.305	6051000	2173300	228310	0.3592	0.0377	2.4	29.8856	29.8856	0.3955	0.3857
4 C Ext. (EtOAc)	594	1.305	2234800	5561	NAR	0.0025	NC	10.0	NC (c)	NC (c)	NC	NC
5 C Ext. (b) (50%DCM/MeOH)	587	1.305	11386000	3532600	175420	0.3103	0.0154	2.4	26.9710	26.9710	0.3797	0.3797
5 C Ext. (50%DCM/MeOH)	615	1.305	20671000	7108200	337240	0.3439	0.0163	2.4	28.9582		0.3802	
	618	1.305	23198000	8050100	439960	0.3470	0.0190	2.4	29.1477	29.0530	0.3816	0.3809
6 C Ext. (EtOAc)	593	1.305	22850000	NAR	13917	NC	0.0006	3.6	NC		0.3909	
•	600	1.305	22232000	NAR	33217	NC	0.0015	3.6	NC	NC	0.3911	0.3910

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Sample not filtered, all others filtered through teflon filters prior to GC injection
(c) Not calculated since GC/MS analysis comfirmed small peak was not MX

Table XVI.17 MX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-dione Displacer (Expt. AD-88-4)

Experiment No. : AD-88-4 MX Desorption Recovery Results

Sample	Mass MX (ug)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (ug)	Net MX Recovered From Carbon (ug) (a)	Min. MX Recovered (%) (b)	Max. MX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	2728.900	107.057	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	7.419	17.420	3.0	0.1391	17.281	0.55	0.63
3 C Ext. (Acetone)	7.471	29.886	2.4	0.1121	29.774	0.95	1.09
5 C Ext. (50%DCM/MeOH)	7.477	29.050	2.4	0.1122	28.938	0.92	1.08
5 C Ext. (d) (50%DCM/MeOH)	7.477	26.971	2.4	0.1122	26.859	0.88	0.99

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Based on calculated mass of initial MX spike.
(c) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.
(d) Sample not filtered, all others filtered through teflon filters prior to GC injection.

NA: Not applicable to blank sample which contained no carbon

Table XVI.18 EMX Recovery Following Desorption Using Various Solvents, Including Benz[a]anthracene-7,12-dione Displacer (Expt. AD-88-4)

Experiment No. : AD-88-4 EMX Desorption Recovery Results

Sample	Mass EMX (µg)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (µg)	Net EMX Recovered From Carbon (µg) (a)	Min. EMX Recovered (%) (b)	Max. EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	11.550	2.2232	10.0	NA	NA	NA	NA
2 C Ext. (EtOAc)	0.019	0.4314	3.0	0.0004	0.431	0.43	3.74
3 C Ext. (Acetone)	0.020	0.3857	2.4	0.0003	0.385	0.38	3.34
5 C Ext. (50%DCM/MeOH)	0.021	0.3797	2.4	0.0003	0.379	0.38	3.29
5 C Ext. (d) (50%DCM/MeOH)	0.021	0.3809	2.4	0.0003	0.381	0.38	3.30

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Based on calculated mass of initial EMX spike.
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.
(d) Sample not filtered, all others filtered through teflon filters prior to GC injection.

NA: Not applicable to blank sample which contained no carbon.
NC: Not calculated due to absence of MX peak.

Table XVI.19 MX and EMX Present Following Initial Adsorption Step (Expt. AD-89-5)

ExperimentNo.: AD-89-5

Water extraction with EtOAc (150ml water; 37, 22, 22 mL EtOAc)
Extracts derivatized dry

Sample	RunNo.	MassMBA (µg)	Area Counts (x10e5)			Area Ratio		MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg.(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA				
1B H2O Ext.	206	1.305	9.02	506	36.5	56.0976	4.0466	640.2	640.2	3.950	3.950
2 H2O Ext.	200	1.305	22.3	1.5	0.432	0.0673	0.0194	0.0784	0.078	0.019	0.019
3 H2O Ext.	201	1.305	40.8	1.7	0.645	0.0417	0.0158	0.0252	0.025	0.019	0.019
4 H2O Ext.	202	1.305	28.3	1	0.223	0.0353	0.0079	0.0137	0.014	0.019	0.019
6 H2O Ext.	203	1.305	32.2	4.58	1.87	0.1422	0.0581	0.2960	0.296	0.022	0.022
6A H2O Ext. "	197 198	1.305 1.305	39.2 69.4	1.95 3.24	0.406 0.705	0.0497 0.0467	0.0104 0.0102	0.0408 0.0348	0.038	0.019 0.019	0.019

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

Spike contained MX:96.9%
EMX:3.1%

Net weight of carbon present in 160 mL serum bottle, corrected for 0.7% moisture content: sample #2-9.6 mg, #3-10.6 mg, #4-10.6 mg, #6-11.0 mg., #6A-11.0 mg.

Table XVI.20 MX and EMX Present Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-dione Displacer (0.005g/25mL) (Expt. AD-89-5)

Experimen No.: AD-89-5

Desorption with various solvents+displacer (25 mL).
Analysis of 10 mL of the (25 mL + 2 to 4 mL) sample (25 mL + 10 mL) blank. Extracts derivatized when dry.

Sample	RunNo.	MassMBA (µg)	Area Counts (x10e5)			Area Ratio		Water Present(mL	MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg.(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA					
1B C Ext. (EtOAc) •	214 234	1.305 1.305	23.700 39.900	79.600 126.000	0.158 0.265	3.3586 3.1579	0.0067 0.0066	10.0 10.0	114.156 106.595	110.376	0.061 0.061	0.061
2 C Ext.(EtOAc) •	204 235	1.305 1.305	39.800 37.700	29.700 28.200	0.384 0.464	0.7462 0.7480	0.0096 0.0123	2.6 2.6	14.206 14.268	14.237	0.049 0.049	0.049
3 C Ext.(Acetone) •	212 237	1.305 1.305	48.600 59.200	16.700 21.900	0.152 1.880	0.3436 0.3699	0.0031 0.0318	0.8 0.8	3.420 3.868	3.644	0.045 0.049	0.047
4 C Ext. (7%MeOH/DCM)	213 238	1.305 1.305	22.400 23.500	37.200 40.900	0.251 0.405	1.6607 1.7404	0.0112 0.0172	0.0 0.0	35.861 38.006	36.933	0.044 0.045	0.045
6 C Ext. C Ext.(50%MeOH/DCM	210 240	1.305 1.305	46.000 26.700	37.100 19.800	2.230 1.210	0.8065 0.7416	0.0485 0.0453	2.8 2.8	16.497 14.147	15.322	0.055 0.054	0.055
6A C Ext. 50%MeOH/DCM, 2 Days	211 239	1.305 1.305	66.200 70.500	177.000 186.000	2.780 2.860	2.6737 2.6383	0.0420 0.0406	2.2 2.2	68.668 67.631	68.149	0.053 0.053	0.053

(a) Not corrected for volume of water present as supernatent during desorption step.

Table XVI.21 MX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-dione Displacer (0.005g/25mL) (Expt. AD-89-5)

Experiment No. : AD-89-5 MX Desorption Recovery Results

Sample	Mass MX (µg)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (µg)	Net MX Recovered From Carbon (µg) (a)	Min. MX Recovered (%) (c)	Max. MX Recovered (%) (d)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	640.200	110.300	10.0	NA	NA	NA	NA
2 C Ext.(EtOAc)	0.079	14.237	2.6	0.0013	14.236	0.46	2.22
3 C Ext.(Acetone)	0.025	3.644	0.6	0.0001	3.644	0.12	0.57
4 C Ext.(b) (7%MeOH/DCM)	0.014	36.933	0.0	0.0000	36.933	1.19	5.77
5 C Ext. (50%MeOH/DCM)	0.296	15.322	2.8	0.0052	15.317	0.49	2.39
6A C Ext. (e) (50%MeOH/DCM,2 Days)	0.038	68.149	2.2	0.0005	68.148	2.19	10.65

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Correction factor as per (a) not applied since water separated into a distinct phase.
(c) Based on calculated mass of initial MX spike.
(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.
(e) This sample was desorbed for 2 days, all others desorbed for 1 day.

NA: Not applicable to sample blank which contained no carbon.

Table XVI.22 EMX Recovery Following Desorption Using Various Solvents Including Benz[a]anthracene-7,12-dione Displacer (0.005g/25mL) (Expt. AD-89-5)

Experiment No. : AD-89-5 EMX Desorption Recovery Results

Sample	Mass EMX (ug)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (ug)	Net EMX Recovered From Carbon (ug) (a)	Min. EMX Recovered (%) (c)	Max. EMX Recovered (%) (d)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	3.850	0.081	10.0	NA	NA	NA	NA
2 C Ext.(EtOAc)	0.019	0.049	2.6	0.0003	0.049	0.49	1.24
3 C Ext.(Acetone)	0.019	0.047	0.8	0.0001	0.047	0.47	1.19
4 C Ext.(b) (7%MeOH/DCM)	0.019	0.045	0.0	0.0000	0.05	0.46	1.14
6 C Ext. (50%MeOH/DCM)	0.022	0.055	2.8	0.0004	0.05	0.55	1.39
6A C Ext. (50%MeOH/DCM, 2 Days)	0.019	0.053	2.2	0.0003	0.05	0.53	1.34

(a) Corrected for volume of water present as supernatant during desorption step.
(b) Correction factor as per (a) not applied since water separated into a distinct phase.
(c) Based on calculated mass of initial EMX spike.
(d) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.
(e) This sample was desorbed for 2 days, all others desorbed for 1 day.

NA: Not applicable to sample blank which contained no carbon.

Table XVI.23 MX and EMX Present Following Initial Adsorption Step (Expt. AD-89-6)

Experiment No.: AD-89-6

Water extraction with EtOAc (150 mL water; 37, 22, 22 mL EtOAc)
Extracts derivatized dry

Sample	Run No.	Mass MBA	Area Counts			Area Ratio		MX (a)	MX Avg. (a)	EMX (a)	EMX Avg.(a)
		(μg)	MBA	MX	EMX	MX/MBA	EMX/MBA	(μg)	(μg)	(μg)	(μg)
1B H2O Ext. (EtOAc)	781	1.595	87432	45164000	298080	516.6	3.4093	7242.3		3.966	
•	783	1.595	87835	47429000	323120	540.0	3.6787	7570.9	7406.6	4.323	4.144
2B H2O Ext. (EtOAc)	782	1.595	115520	59282000	445290	513.2	3.8547	7194.8		4.582	
•									7194.8		4.582
3 H2O Ext. (EtOAc)	781	1.595	1006200	555620	24876	0.5522	0.0247	3.8		0.024	
•	784	1.595	133320	121330	NAR	0.9101	NC	9.6	6.691	NC	0.024
4 H2O Ext. (EtOAc)	782	1.595	1401800	457350	4883	0.3263	0.0035	1.5		0.023	
•	785	1.595	990710	356610	21946	0.3600	0.0222	1.8	1.633	0.024	0.023
5 H2O Ext. (EtOAc)	786	1.595	1679400	554480	8329	0.3302	0.0050	1.5		0.023	
•	786	1.595	690900	287780	NAR	0.4165	NC	2.3	1.909	NC	0.023
6 H2O Ext. (EtOAc)	787	1.595	823400	476290	1865	0.5784	0.0023	4.1		0.022	
•	787	1.595	402800	299010	24846	0.7423	0.0617	6.6	5.348	0.027	0.025
7.H2O Ext. (EtOAc)	788	1.595	1413600	752250	62961	0.5322	0.0445	3.6		0.025	
•	788	1.595	480480	351540	NAR	0.7316	NC	6.4	4.970	NC	0.025
8 H2O Ext. (EtOAc)	789	1.595	513350	264570	3082	0.5154	0.0060	3.4		0.023	
•	789	1.595	282860	183980	NAR	0.6504	NC	5.1	4.249	NC	0.023

(a) Based upon extraction of 150 mL sample, corrected to total bottle volume of 160 mL.

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

Spike contained MX:96.9%
EMX:3.1%

Table XVI.24 MX and EMX Present Following Desorption at 70°C Using Various Solvents (Expt. AD-89-6)

ExperimentNo.: AD-89-6

Desorption with various solvents (100 mL) @ 70 C.
Analyzed 50 mL of these solutions (samples-100 mL solvent +3 to 4 mL water; blank-100 mL solvent +10 mL water)
Extracts derivatized dry

Sample	RunNo.	MassMBA (µg)	Area Counts			Area Ratio		Water Present(mL	MX (a) (µg)	MX Avg. (a) (µg)	EMX (a) (µg)	EMX Avg.(a) (µg)
			MBA	MX	EMX	MX/MBA	EMX/MBA					
1 C Ext. (EtOAc) *	770 792	1.595 1.595	22338 9265	655850 303480	(b) (b)	29.3629 32.7555	NC NC	10.0 10.0	840.1 938.3	889.2	NC NC	NC
2 C Ext. (7%MeOH/DCM) *	771 791	1.595 1.595	2537000 583380	23387000 7805800	30042 9401	9.2184 13.3803	0.0118 0.0161	10.0 10.0	257.3 377.7	317.5	.047 .048	.048
3 C Ext. (EtOAc) (b,c)	772 793	1.595 1.595	1951700 1327900	5131400 3771900	414100 293290	2.6292 2.8405	0.2122 0.2209	4.7 4.7	63.4 69.2	66.3	.077 .079	.078
4 C Ext. (EtOAc) *	773 794	1.595 1.595	265280 90377	2018300 944830	(b) (b)	7.6082 10.4543	NC NC	4.7 4.7	200.5 278.9	239.7	NC NC	NC
5 C Ext. (Acetone) *	774 795	1.595 1.595	1800600 422450	4766700 1726400	38477 14742	2.6473 4.0866	0.0214 0.0349	3.9 3.9	63.4 102.7	83.1	.046 .048	.047
C Ext.(7%MeOH/DCM) (d,e)	775	1.595	1661900	10599000	210300	6.3776	0.1265	0.0	159.1	159.1	.060	.060
7 C Ext.(7%MeOH/DCM) *	776 796	1.595 1.595	812790 282630	10286000 4987800	59272 109390	12.6552 17.6478	0.0729 0.3870	0.0 0.0	324.3 455.6	389.9	.051 .107	.079
C Ext.(50%MeOH/DCM) *	777 797	1.595 1.595	943940 332600	5658700 2747500	NAR NAR	5.9948 8.2607	NC NC	2.4 2.4	152.6 213.7	183.2	NC NC	NC

NAR: No area counts recorded at specified retention time.
NC: Not calculated since no area counts recorded.

(a) Not corrected for volume of water present as supernatant during desorption step.
(c) EMX area counts could not be properly delineated due to interfering peak at same retention time.
(d) Sample spilled while concentrating under nitrogen; subsequent recovery is low.
(e) Approx. 1 mg carbon lost during removal of aqueous phase prior to desorption.
(f) Vial #6 broken after first injection.

Table XVI.25 MX Recovered Following Desorption at 70°C Using Various Solvents (Expt. AD-89-6)

Experiment No. : AD-89-6 MX Desorption Recovery Results

Sample	Mass MX (ug)		Water Present In Carbon Extr. (mL)	MX Pres. In Extran. Water (ug)	Net MX Recovered From Carbon (ug) (a)	Min. MX Recovered (%) (c)	Max. MX Recovered (%) (d)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	7300.700	889.200	10.0	NA	NA	NA	NA
2B C Ext.(7%MeOH/DCM)	7300.7 (b)	317.5 (c)	0.0	NA	NA	NA	NA
4 C Ext. (EtOAc)	1.833	239.700	4.7	0.0480	239.652	1.5	3.3
5 C Ext. (Acetone)	1.909	83.100	3.9	0.0465	83.053	0.5	1.1
7 C Ext. (7%MeOH/DCM)	4.970	389.900	0.0	0.0000	389.900	2.5	5.3
8 C Ext. (50%MeOH/DCM)	4.249	183.200	2.4	0.0637	183.136	1.2	2.5

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Initial values for samples 1B and 2B are represented as an average since both initial water extractions were done with EtOAc.
(c) Final values for samples 1B and 2B differ due to differences in extraction efficencies for the two solvent systems.
(d) Based on mass of MX present in sample blank (containing no carbon) following 1 day equilibration.

NA: Not applicable to blank sample which contained no carbon

Table XVI.26 EMX Recovered Following Desorption at 70°C Using Various Solvents (Expt. AD-89-6)

Experiment No. : AD-89-6 EMX Desorption Recovery Results

Sample	Mass EMX (ug)		Water Present In Carbon Extr. (mL)	EMX Pres. In Extran. Water (ug)	Net EMX Recovered From Carbon (ug) (a)	Min. EMX Recovered (%)	Max.EMX Recovered (%) (c)
	Initial H2O Extr.	Final Carbon Extr.					
1B C Ext. (EtOAc)	4.35	NVD	10.0	NA	NA	NA	NA
B C Ext.(7%MeOH/DCM)	4.35 (b)	0.043	0.0	NA	NA	NA	NA
4 C Ext. (EtOAc)	0.023	NVD	4.7	NVD	NVD	NVD	NVD
5 C Ext. (Acetone)	0.023	0.047	3.9	0.0006	0.046	0.0	1.1
7 C Ext. (7%MeOH/DCM)	0.025	0.079	0.0	0.0000	0.079	0.0	1.8
8 C Ext. (50%MeOH/DCM)	0.023	NVD	2.4	NVD	NVD	NVD	NVD

(a) Corrected for volume of water present as supernatent during desorption step.
(b) Values for samples 1B and 2B are the same since both initial water extractions were done with EtOAc.
(c) Based on mass of EMX present in sample blank (containing no carbon) following 1 day equilibration.

NA: Not applicable to blank sample which contained no carbon
NVD: No value determined.